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CONTENTS.

A. SMITS: "On the introduction of the conception of the solubility of metal ions with electromotive equilibrium". (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 2.

A. SMITS: "On the course of the P,T-curves for constant concentration for the equilibrium solid-fluid". (Communicated by Prof. J. D. VAN DER WAALS), p. 9.

J. MOLL VAN CHARANTE: "The formation of salicylic acid from sodium phenolate". (Communicated by Prof. A. P. N. FRANCHIMONT), p. 20.

F. M. JAEGER: "On the crystal-forms of the 2,4 Dinitroaniline-derivatives, substituted in the NH_2-group". (Communicated by Prof. P. VAN ROMBURGH), p. 23.

F. M. JAEGER: "On a new case of form-analogy and miscibility of position-isomeric benzene-derivatives, and on the crystalforms of the six Nitrodibromobenzenes". (Communicated by Prof. A. F. HOLLEMAN), p. 26.

H. J. HAMBURGER and SVANTE ARRHENIUS: "On the nature of precipitin-reaction", p. 33.

J. STEIN: "Observations of the total solar eclipse of August 30, 1905 at Tortosa (Spain)". (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN), p. 45.

J. J. VAN LAAR: "On the osmotic pressure of solutions of non-electrolytes, in connection with the deviations from the laws of ideal gases". (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM), p. 53.

Chemistry. — "*On the introduction of the conception of the solubility of metal ions with electromotive equilibrium.*" By Dr. A. SMITS. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM).

(Communicated in the meeting of April 27, 1906.)

If a bar of NaCl is placed in pure water or in a dilute solution, the NaCl-molecules will pass into the surrounding liquid, till an equilibrium has been established; then the molecular thermodynamic potential of the Na Cl in the bar has become equal to that of the Na Cl in the solution.

As known, this equilibrium of saturation, represented by the equation:

$$\mu_{NaCl} = \mu'_{NaCl}$$

is characterized by the fact that per second an equal number of molecules pass from the bar into the solution, as from the solution into the bar.

We shall call this equilibrium a purely chemical equilibrium. It is true that in solution the Na Cl-molecules split up partially into particles charged either with positive or negative electricity, which are in equilibrium with the unsplit molecules, but for the heterogeneous equilibrium solid-liquid under consideration this is not of *direct* importance.

If, however, we immerge a metal e. g. *Zn* into a solution of a salt of this metal, e. g. $ZnSO_4$, we observe a phenomenon strongly deviating from the one just discussed, which according to our present ideas may be accounted for by the fact that a metal does not send out into the solution *electrically neutral* molecules as a salt, but exclusively *ions with a positive charge.*

If the particles emitted by the bar of zinc were *electrically neutral,* then the zinc would continue to be dissolved till the molecular thermodynamic potential of the zinc in the bar of zinc had become equal to that of the zinc in the solution, in which case the equation:

$$\mu_{zn} = \mu'_{zn}$$

would hold.

This, however, not being the case, and the emitted *Zn*-particles being electro-positive, an equilibrium is reached *long* before the thermodynamic potential of the zinc-particles with the positive electric charge in the solution has become equal to that of the zinc in the bar of zinc with the negative electric charge. That in spite of this an equilibrium is possible, is due to the fact that an electrical phenomenon acts in conjunction with the chemical phenomenon.

The zinc emitting positive *Zn*-ions, the surrounding solution becomes electro-positive, and the zinc itself electro-negative. As known, this gives rise to the formation of a so-called electric double-layer in the bounding-layer between the metal and the electrolyte, consisting of positive *Zn*-ions on the side of the electrolyte and an equivalent amount of negative electricity or electrons in the metal.

By the formation of this electric double-layer an electric potential difference between metal and electrolyte is brought about, which at first increases, but very soon becomes constant. This takes place when the potential difference has become great enough to prevent the further solution of the *Zn*-ions.

In order to compute the potential difference between the metal and the solution, we shall apply the principle of the virtual displacement, as has been done before by Mr. VAN LAAR.[1])

If we have to do with a purely chemical equilibrium then with virtual displacement of this equilibrium the sum of the changes of molecular potential will be $= 0$, which is expressed by the equation of equilibrium:

$$\Sigma(\mu_1 \, dn_1) = 0.$$

If the equilibrium is a purely electrical equilibrium then with a virtual displacement of this equilibrium the sum of the changes of electric energy will be $= 0$.

If however we have an equilibrium that is neither purely chemical, nor purely electrical, but a combination of the two, as is the case with electromotive equilibrium, then with virtual displacement of this equilibrium, the sum of the changes of the molecular-potential $+$ the sum of the changes of the electric energy will have to be $= 0$.

If we represent the mol. potential of the *Zn*-ions by $\overset{+}{\mu}_{zn}$ in case of electromotive equilibrium, we know that $\overset{+}{\mu}_{zn}$ is *much* smaller than μ_{zn} or the mol. potential of the zinc in the bar of zinc.

If we now suppose that a *Zn*-ion emitted by the zinc virtually carries a quantity of electricity *de* from the metal towards the solution, then this quantity of electricity being carried by a ponderable quantity $\frac{de}{v\varepsilon}$ when $v =$ valency of the metal and $\varepsilon =$ the charge of a univalent ion, the increase of the thermodynamic potential during this process will be equal to

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[1]) Chem. Weekbl. N°. 41, 1905.

$$\frac{\overset{+}{\mu}_{zn} - \mu_{zn}}{v\varepsilon}\, de$$

which increase is negative, because $\mu_{zn} > \overset{+}{\mu}_{zn}$.

In the virtual displacement of the quantity of electricity de from the metal towards the solution the change of the thermodynamic potential is not the only one that has taken place during this process.

If we call the electric potential of the solution V_e and that of the zinc V_m, we know that in the above case $V_e > V_m$ and $V_e - V_m = \Delta$ indicates the potential difference of the electrolyte and the metal. With the virtual displacement of the quantity of electricity de from the metal to the electrolyte this quantity has undergone an electrical potential increase Δ, and so the electric energy has increased with $\Delta\, de$.

From the principle of virtual displacement follows that with electromotive equilibrium

$$\frac{\overset{+}{\mu}_{zn} - \mu_{zn}}{v\,\varepsilon}\, de + \Delta\, de = 0, \quad \ldots\ldots\ldots \quad (1)$$

or

$$\Delta = -\frac{\overset{+}{\mu}_{zn} - \mu_{zn}}{v\,\varepsilon} \quad \ldots\ldots\ldots \quad (2)$$

Now we know that the mol. thermodyn. potential of a substance may be split up as follows:

$$\mu = \mu' + R\,T\,ln\,C$$

where in diluted states of matter μ' may be called a function of the temperature alone.

In non-diluted states however, μ' depends also somewhat on the concentration.

If we now apply this splitting up also to equation (2), we get:

$$\Delta = -\frac{(\overset{+}{\mu'}_{zn} - \mu_{zn}) + R\,T\,ln\,C}{v\,\varepsilon} \quad \ldots\ldots \quad (3)$$

where C represents the concentration of the Zn-ions in the electrolyte.

If we now put:

$$\frac{\mu_{zn} - \overset{+}{\mu'}_{zn}}{R\,T} = ln\,K \quad \ldots\ldots\ldots \quad (4)$$

we may say of this K that for diluted states of matter it will only

depend on the temperature, and will therefore be a constant at constant temperature.

From equation (3), (4) follows

$$\Delta = \frac{RT}{\nu\varepsilon} ln \frac{K}{C} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Mr. VAN LAAR already pointed out that this equation, already derived by him in the same way is identical with that derived by NERNST $\Delta = \frac{RT}{\nu\varepsilon} ln \frac{P}{p}$, in which therefore $\frac{P}{p}$ stands instead of $\frac{K}{C}$. P represents the "elektrolytische Lösungstension" of the metal, and p the "osmotic pressure" of the metal-ions in the solution.

Rejecting the osmotic phenomenon as basis for the derivation of the different physico-chemical laws, we must, as an inevitable consequence of this, also abandon the osmotic idea "elektrolytische Lösungstension" introduced by NERNST.

The principal purpose of this paper is to prove that there is not any reason to look upon this as a disadvantage, for, when we seek the physical meaning of the quantity K in equation (5), it can be so simply and sharply defined, that when we take the theory of the thermodynamic potential as foundation, we do not lose anything, but gain in every respect.

In order to arrive at the physical meaning of the quantity K, we put for a moment

$$C = K$$

from which follows

$$\Delta = 0.$$

From this follows that there is a theoretical possibility to give such a concentration to the metal-ions in a solution that when we immerge the corresponding metal in it, *neither the metalnor the solution gets electrically charged.*

How we must imagine this condition is shown by equation (2). Let us put there $\Delta = 0$, then follows from this for an arbitrary metal

$$\mu_m = \overset{+}{\mu}_m$$

or in words the molecular potential of the metal in the bar is equal to that of the metal-ions in the solution.

So it appears that we have here to do with an equilibrium which is perfectly comparable with that between the Na Cl in the bar Na Cl, and the salt in the solution.

The only difference is this that the molecules of a salt in solution are neutrally electric, whereas the metal particles in solution are charged with positive electricity, hence the physical meaning of the equation $\mu_m = \overset{+}{\mu}_m$ is simply this that in *absence* of a potential difference, per second an equal number of metal particles are dissolved as there are deposited.

If we express this in the most current terms, we may say, that when $C = K$ the metal-ions have reached their *concentration of saturation*, and that K therefore represents the *solubility of the metal-ions*.

To prevent confusion, it will be necessary to point out that the fact that the dissolved metal-particles in equilibrium with the solid metal have an electric charge, is attended by peculiarities which are met with in no other department.

Thus it will appear presently that in every solution of copper-sulphate which is not extremely diluted, the concentration of the copper-ions is supersaturated with respect to copper. Yet such a copper-sulphate-solution is in a perfectly stable condition, because the copper-ions constitute a part of the following homogeneous equilibrium,

$$CuSO_4 \rightleftarrows Cu^{\cdot\cdot} + SO_4''$$

which is perfectly stable as long as the solution is unsaturate or is just saturate with $CuSO_4$-molecules.

If we now, however, insert a copper bar into the solution, the condition changes, because the Cu-ions which were at first only in equilibrium with the $CuSO_4$-mols and with the SO_4''-ions, must now also get into equilibrium with the copper bar, and, the concentration of the Cu-ions with respect to copper being strongly supersaturate, the Cu-ions will immediately deposit on the copper, till the further depositing is prevented in consequence of the appearance of a double layer.

We shall further see that in the most concentrated solution of a zinc-salt the concentration of the zinc-ions always remains below the concentration of saturation, which appears immediately when we immerge a zinc-bar into such a solution; the zinc emits zinc particles with a positive charge into the solution, till the appearance of the electric double layer puts a stop to the phenomenon of solution.

In order to find the values of K for different metals we make use of the observed potential difference with a definite value of C.

We know the potential difference at 18° and with normal concentration of the ions, i. e. when solutions of 1 gr. aeq. per liter of water are used. These potential differences are called electrode potentials, and will be denoted here by Δ_0.

If we express the concentration in the most rational measure, viz. in the number of gr. molecules dissolved substance divided by the total number of gr. molecules, we may write for the concentration of 1 gr. eq. per liter

$$\frac{1}{55{,}5\ v + 1}$$

in which v represents the valency of the metal. In this it has been further assumed, that the dissociation is total, and the association of the water molecules has not been taken into account.

If we now write the equation for the electrode potential of an arbitrary metal, we get:

$$\Delta_0 = \frac{RT}{v\varepsilon} ln \frac{K}{\frac{1}{55{,}5\ v + 1}}$$

or

$$\Delta_0 = \frac{RT}{v\varepsilon} ln\ K(55{,}5\ v + 1)$$

If we use ordinary logarithms for the calculation, we get:

$$\Delta_0 = \frac{RT}{v\varepsilon \times 0{,}4343} log\ K(55{,}5\ v + 1)$$

If we now express R in electrical measure, then

$$\Delta_0 = \frac{0{,}000198}{v} T log\ K(55{,}5\ v + 1)$$

and for $t = 18$ or $T = 291°$

$$\Delta_0 = \frac{0{,}0578}{v} log\ K(55{,}5\ v + 1)$$

If we now calculate the quantity $log\ K$ by means of this equation from the observed values of Δ_0, we get the following. (See table p. 8).

In the succession in which the metals are written down here, the value of Δ_0 decreases and with it the value of $log\ K$.

For the metals down to *Fe* (*Fe* included) $log\ K$ is greater than zero, so K greater than 1.

Now we know that C for a solution is always smaller than 1; hence K will always be larger than C for the metals mentioned, and as K denotes the concentration of saturation of the metal-ions,

Values of $\log K$ at 18°.

metal ion	Δ_0	$\log K$	metal ion	Δ_0	$\log K$
$K^{\cdot}$	(+ 2,92) [1]	(+48,77)	$Co^{\cdot\cdot}$	— 0,045	— 1,805 2
$Na^{\cdot}$	(» 2,54)	(42,19)	$Ni^{\cdot\cdot}$	» 0,049	— 1,872 × 2
$Ba^{\cdot\cdot}$	(» 2,54)	(42,92 × 2)	$Sn^{\cdot\cdot}$	< » 0,085	< — 2,49 × 2
$Sr^{\cdot\cdot}$	(» 2,49)	(42,06 × 2)	$Pb^{\cdot}$	» 0,13	— 3 27 × 2
$Ca^{\cdot}$	(» 2,28)	(38,42 × 2)	$H^{\cdot}$	» 0,28	— 6,6
$Mg^{\cdot}$	» 2,26	38,07 × 2	$Cu^{\cdot\cdot}$	» 0,61	— 11,58 × 2
$Al^{\cdot\cdot\cdot}$	» 1,00	16,56 × 3	$Bi^{\cdot\cdot\cdot}$	< » 0,67	< — 12 33 × 3
$Mn^{\cdot\cdot}$	» 0,80	12,81 × 2	$Hg_2^{\cdot\cdot}$	» 1,03	— 18,84 × 2
$Zn^{\cdot\cdot}$	» 0,49	7,45 × 2	$Ag^{\cdot}$	» 1,05	— 19,92
$Cd^{\cdot\cdot}$	» 0,14	1,39 × 2	$Pd^{\cdot\cdot}$	» 1,07	— 19,03 × 2
$Fe^{\cdot\cdot}$	» 0,063	0,065 × 2	$Pt^{\cdot\cdot\cdot\cdot}$	» 1,14	— 20,62 × 4
$Tl^{\cdot\cdot}$	» 0,045	— 0,245 × 2	$Au^{\cdot\cdot\cdot}$	» 1,36	— 26,27 × 3

the metal-ions will not yet have reached their concentration of saturation even in the most concentrated solutions of the corresponding metal-salts. Hence, when the corresponding metal is immerged, metal ions will be dissolved, in consequence of which the solution will be charged with positive and the metal with negative electricity.

Theoretically the case, in which K would always be smaller than C, can of course not occur. If $\log K$ is smaller than zero, so K smaller than 1, then the theoretical possibility is given to make the potential difference between the metal and the corresponding salt solution reverse its sign, which reversal of sign of course takes place through zero. Whether it will be possible to realize this, depends on the solubility of the salt.

If we now take the metal copper as an example, we see that for this metal K has the very small value of 10^{-23}. On account of this very small value of K, C is greater than K in nearly all copper-salt-solutions, or in other words the concentration of the Cu-ions is greater than the concentration of saturation. Hence copper-ions are deposited on a copper bar, when it is immerged, in consequence which the bar gets charged with positive, and the solution with negative electricity.

But however small K may be, it will nearly always be possible to

[1]) The values of Δ_0 between parentheses have been calculated from the quantity of heat.

make C smaller than K. In a copper-salt-solution e.g. this can very easily be done, as is known, by addition of KCN, which in consequence of the formation of the complex-ions $[Cu_2(CN)_4]''$, causes copper-ions to be extracted from the solution. The solution, which at first had a negative charge compared with the metal copper, loses this charge completely by the addition of KCN, and receives then a positive charge.

In the above I think I have demonstrated the expediency of replacing the vague idea "elektrolytische Lösungs-tension" by the sharply defined idea solubility of metal ions.

Amsterdam, April 1906. *Anorg. Chem. Lab. of the University.*

Physics. — *"On the course of the P,T-curves for constant concentration for the equilibrium solid-fluid."* By Dr. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS.)

(Communicated in the meeting of April 27, 1906).

In connection with my recent investigations it seemed desirable to me to examine the hidden connection between the sublimation and melting-point curves for constant concentration, more particularly when the solid substance is a dissociable compound of two components. This investigation offered some difficulties, which I, however, succeeded in solving by means of data furnished by a recent course of lectures giving by Prof. VAN DER WAALS. Though his results will be published afterwards, Prof. VAN DER WAALS allowed me, with a view to the investigations which are in progress, to use that part that was required for my purpose.

In his papers published in 1903 in connection with the investigation on the system ether-anthraquinone [1]) VAN DER WAALS also discussed the P, T-lines for constant x for the equilibrium between solid-fluid [2]), and more particularly those for concentrations in the immediate neighbourhood of the points p and q, where saturated solutions reach their critical condition.

Then it appeared that the particularity of the case involved also particularities for the P, T-line, so that the course of the P, T-line as it would be in the usual case, was not discussed.

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[1]) These Proc. VI p. 171 and p, 484 Zeitschr. f. phys. Chem. **51**, 193 and **52**, 587 (1905).

[2]) These Proc. VI p. 230 and p. 357.

If we start from the differential equation in p,x and T derived by VAN DER WAALS (Cont. II, 112).

$$V_{sf}\,dp = (x_s - x_f)\left(\frac{\partial^2\zeta}{\partial x^2{}_f}\right)_{PT} dx_f + \frac{W_{sf}}{T}\,dT \quad . \quad . \quad . \quad (1)$$

we get from this for constant x that

$$V_{sf}\,dp = \frac{T}{W_{sf}}\,dT \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

or

$$T\left(\frac{dp}{dT}\right)_{xf} = \frac{W_{sf}}{V_{sf}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If we now multiply numerator and denominator by $\frac{\partial^2\psi}{\partial v_f{}^2}$ as will prove necessary for simplifying the discussion, we get:

$$T\left(\frac{dp}{dT}\right)_{xf} = \frac{\frac{\partial^2\psi}{\partial v_f{}^2}\cdot W_{sf}}{\frac{\partial^2\psi}{\partial v_f{}^2}\cdot V_{sf}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

In order to derive the course of the P, T-lines from this equation, the loci must be indicated of the points for which the numerator, resp. the denominator = zero, and at the same time the sign of these quantities within and outside these loci must be ascertained.

In the v,x-fig. 1 the lines ab and cd denote the two connodal lines at a definite temperature. The line P_SQ_S whose $x = x_s$ the concentration of the solid compound AB cuts these connodal lines and separates the v,x-figure into two parts, which call for a separate discussion.

If P_S denotes the concentration and the volume of the solid compound at a definite temperature, then the isobar $MQRDD'R'Q'N$ of the pressure of P_S will cut the connodal lines in two points Q and Q', which points indicate the fluid phases coexisting with the solid substance AB, and therefore will represent a pair of nodes.

The points for which $\frac{\partial^2\psi}{\partial v^2} = 0$ or $-\frac{dp}{\partial v} = 0$ are situated where the isobar has a vertical tangent, so in the points D and D' as VAN DER WAALS [1]) showed already before. In D the isobar passes through the minimum pressure of the mixture whose $x = x_D$, and so it has there an element in common with the isotherm of this concentration. In D' however, the isobar passes through the maxi-

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[1]) These Proc. IV p. 455.

mum pressure of the mixture whose $x = x_{D'}$, and will therefore have an element in common with the isotherm of the concentration $x_{D'}$.

As for the sign of $\frac{\partial^2 \psi}{\partial v^2}$ we may remark that it is positive outside the points D and D' and negative inside them.

The ordinary case being supposed in the diagram, viz. $V_s < V_f$, we may draw two tangents to the above mentioned isobar from the point P_s with the points of contact R and R'. These points of contact now, indicate the points where the quantity $V_{sf} = 0$, as VAN DER WAALS [1]) showed.

This quantity is represented by the equation:

$$V_{sf} = (V_s - V_f) - (x_s - x_f)\left(\frac{dv_f}{dx_f}\right)_{PT} \quad . \quad . \quad . \quad . \quad (5)$$

and denotes the decrease of volume per molecular quantity when an infinitely small quantity of the solid phase passes into the coexisting fluid phase at constant pressure and temperature.

For the case that the coexisting phase is a vapour phase, V_{sf} is negative, but this quantity can also be positive, and when the pressure is made to pass through all values, there is certainly once reversal of sign, for the case $V_f > V_s$ even twice.

To elucidate this Prof. VAN DER WAALS called attention to the geometrical meaning of V_{sf}.

Let us call the coordinates of the fluid phases Q' coexisting with P_s, V_f and X_f and let us draw a tangent to the isobar in Q'. Then $P_s\ P'$ will be equal to V_{sf} if P' is the point where this tangent cuts the line drawn parallel to the axis of v through P_s.

If the point P' lies above P_s, V_{sf} is negative, and if P' lies under P_s, then V_{sf} is positive. For the case that the tangent to the isobar passes through P_s, which is the case for the points R and R', $V_{sf} = 0$.

In this way it is very easy to see that for the points outside those for which $V_{sf} = 0$, the value of V_{sf} is negative, and for the points within them, V_{sf} is positive, but this latter holds only till the points D and D' have been reached, where $V_{sf} = \infty$. Between D and D', V_{sf} is again negative. The transition from positive to negative takes therefore place through ∞.

As each of the lines of equal pressure furnishes points where

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[1]) These Proc. VI, p. 234.

$\frac{\partial^2\psi}{\partial v^2} = 0$ and $V_{sf} = 0$, when connecting the corresponding points we obtain loci of these points, indicated by lines.

As, however, we simplify the discussion, as VAN DER WAALS has shown, when we consider the quantity $\frac{\partial^2\psi}{\partial v_f^2} . V_{sf}$ instead of the quantity V_{sf}, because this product can never become infinitely great and is yet zero when $V_{sf} = 0$, the locus of the points where $\frac{\partial^2\psi}{\partial v_f^2} . V_{sf} = 0$ is given in fig. 1.

We know then too that this quantity on the left of the line of the compound is negative outside this locus, and positive within it.

Further the locus of $\frac{\partial^2\psi}{\partial v^2} = 0$ is indicated, and we see that these two lines intersect at the point where they pass through the line of the compound.

In his lectures VAN DER WAALS has lately proved in the following way that this must necessarily be so: If we write for $\frac{\partial^2\psi}{\partial v_f^2} . V_{sf}$

$$(V_s - V_f)\frac{\partial^2\psi}{\partial v_f^2} + (x_s - x_f)\frac{\partial^2\psi}{\partial v_f \partial x_f} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

we see that when this quantity $= 0$, and when at the same time $x_s = x_f$:

$$(V_s - V_f)\frac{\partial^2\psi}{\partial v_f^2} = 0$$

or

$$\frac{\partial^2\psi}{\partial v_f^2} = 0.$$

I, too, had already arrived at the conclusion that in the left half of our diagram the two loci mentioned had interchanged places, by assuming that there existed a three-phase equilibrium also on the right, and by drawing the corresponding isobar $M_1 Q_1 D_1 R_1 R_1' D_1' Q_1' N'$. It appears then that here the points R_1 and R_1' lie within the points D_1 and D_1', which points to a reversed situation (compared with the left half) of the loci $\frac{\partial^2\psi}{\partial v_f^2} . V_{sf} = 0$ and $\frac{\partial^2\psi}{\partial v_f^2} = 0$. VAN DER WAALS has also given this graphical proof.

As for the sign of the quantity $\frac{\partial^2\psi}{\partial v_f^2}$ on the right of the line

of the compound also there it is negative outside, positive inside the first mentioned locus.

Before proceeding to my real subject, I shall, for the sake of completeness, first call attention to the fact that the spinodal curve, for which the equation:

$$\frac{\partial^2\psi}{\partial x^2} - \frac{\left(\frac{\partial^2\psi}{\partial x \partial v}\right)}{\frac{\partial^2\psi}{\partial v^2}} = 0 \quad \text{or} \quad \frac{\partial^2\zeta}{\partial x^2{}_p} = 0 \quad . \quad . \quad . \quad . \quad . \quad (7)$$

holds, lies entirely ontside the locus $\frac{\partial^2\psi}{\partial v^2} = 0$. VAN DER WAALS [1]) proved this in the following way:

On the spinodel curve $\frac{\partial^2\psi}{\partial x^2}$ and $\frac{\partial^2\psi}{\partial v^2}$ must both be positive, and so also $\left(\frac{\partial^2\psi}{\partial x \partial v}\right)^2$. As $\frac{\partial^2\psi}{\partial v^2} = -\frac{\partial p}{\partial v}$ is positive outside the line for which $\frac{\partial^2\psi}{\partial v^2} = 0$, the spinodal line will always have to lie outside the curve $\frac{\partial^2\psi}{\partial v^2} = 0$.

That the spinodal curve which coming from the left, runs between the lines $\frac{\partial^2\psi}{\partial v^2{}_f} . V_{sf} = 0$ and $\frac{\partial^2\psi}{\partial v^2{}_f} = 0$, cuts the line for $\frac{\partial^2\psi}{\partial v_f{}^2}$. $V_{sf} = 0$ on the left of the line of the compound in two points q_1 and q_2 which will be discussed afterwards, follows from this, that *on* the line of the compound $\frac{\partial^2\psi}{\partial v_f{}^2} . V_{sf} = 0$ coincides with $\frac{\partial^2\psi}{\partial v_f{}^2} = 0$ and that the line $\frac{\partial^2\psi}{\partial v_f{}^2}$ always lies within the spinodal line, whereas on the right of the line of the compound $\frac{\partial^2\psi}{\partial v_f{}^2}$. $V_{sf} = 0$ lies within the line $\frac{\partial^2\psi}{\partial v_f{}^2} = 0$.

When we start from the maximum temperature of sublimation, we get now v,x-lines which have been indicated by T_1, T_2, T_3 and T_4 in fig. 1 for the equilibria between solid-fluid according to the equation [2])

$$\frac{dv_f}{dx_f} = -\frac{\left[(v_s - v_f)\frac{\partial^2\psi}{\partial v_f . \partial x_f} + (x_s - x_f)\frac{\partial^2\psi}{\partial x^2{}_f}\right]}{\frac{\partial^2\psi}{\partial v^2{}_f} . v_{sf}} . \quad . \quad . \quad . \quad (8)$$

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[1]) loc cit.

[2]) These Proc. VI, p. 489.

The v,x-curve denoted by T_1, relating to the *maximum temperature of sublimation*, consists of two branches, which pass continuously into each other. The points of intersection with the connodal line $a\,b$ indicate the vapour phases and those with the connodal line $c\,d$ the liquid phases. In this way we get two pairs of fluid phases which can coexist with the solid compound at the same temperature.

At the place where the two branches of the v,x-line cut the locus $\frac{\partial^2\psi}{\partial v^2{}_f}\,V_{sf}\,,\ \frac{\partial v}{\partial x}=\infty$.

With increase of temperature these branches draw nearer to each other, and when they would *touch*, intersection takes place; this is here supposed to take place for the v,x-line denoted by T_2. This point of intersection is the point q_1, it lies therefore both on the spinodal curve and on the curve $\frac{\partial^2\psi}{\partial v^2{}_f}\,.\,V_{sf}=0$.

If we now proceed to higher temperatures, detachment takes place, and the v,x-figure consists of two separate branches, one of which, viz. the vapour branch is closed. This case is represented by the v,x-line T_3, for which it is also assumed, that this temperature is the *minimum-melting point* of the compound, which follows from the fact that the liquid branch of the v,x-line T_3, simultaneously cuts the connodal line $c\,d$ and the line of the compound.

With rise of temperature the closed v,x-line contracts, and the corresponding liquid branch descends. The points of intersection of the closed vapour branch and the liquid branch with the connodal curves draw nearer and nearer to each other, and at a certain temperature the two branches will show contact. The closed vapour branch touches the connodal curve $a\,b$ and the liquid branch the connodal curve $c\,d$. This is represented by the v,x-figure T_4, which represents the condition at the *maximum-threephase-temperature*, at which the points of contact on the connodal curves and the point for the solid substance must lie in one line.

At higher temperature no three phase equilibrium is possible any longer, and both the closed vapour branch and the liquid branch have got detached from the connodal curves. The liquid branch descends lower and lower, and the closed branch contracts more and more, and vanishes as a point in q_2, where the upper branch of the spinodal curve and the curve $\frac{\partial^2\psi}{\partial v^2{}_f}\,V_{sf}=0$ intersect.

If we now also indicate the locus of the points where $\frac{\partial^2\psi}{\partial v f^2}\,.\,W_{sf}=0$

the peculiarities of the course of the *PT*-lines may easily be derived by means of the foregoing.

For the determination of the last mentioned locus, we start from the equation:

$$W_{sf} = \left[p + \left(\frac{\partial \varepsilon_f}{\partial v_f}\right)_{T,x}\right] V^{sf} + (\varepsilon_{sf})_v \quad . \quad . \quad . \quad . \quad (9)$$

The factor of V_{sf} being naturally positive and $(\varepsilon_{sf})_v$ being always negative, W_{sf} can only be equal to zero in a point x where V_{sf} is positive, so between the loci where $V_{sf}=0$ and $\frac{\partial^2\psi}{\partial v_f^2}=0$.

Further it is now easy to understand that at the same time with V_{sf} the quantity W_{sf} will become infinitely great, there where $\frac{\partial^2\psi}{\partial v_f^2}=0$. In order to avoid this complication VAN DER WAALS has multiplied the quantity W_{sf} by $\frac{\partial^2\psi}{\partial v_f^2}$ as equation (4) shows; the obtained product never becomes infinitely great now.

If we multiply equation (9) by $\frac{\partial^2\psi}{\partial v_f^2}$, we get:

$$\frac{\partial^2\psi}{\partial v_f^2} \cdot W_{sf} = \left[p + \left(\frac{\partial \varepsilon_f}{\partial v_f}\right)_{T,x}\right] \frac{\partial^2\psi}{\partial v_f^2} \cdot V_{sf} + \frac{\partial^2\psi}{\partial v_f^2} (\varepsilon_{sf})_v \quad . \quad . \quad (10)$$

Now we know that the locus for $\frac{\partial^2\psi}{\partial v_f^2} \cdot W_{sf} = 0$ will have to lie between that for $\frac{\partial^2\psi}{\partial v_f^2} \cdot V_{sf} = 0$ and for $\frac{\partial^2\psi}{\partial v_f^2} = 0$, as drawn in fig. 1, which compels us to make $\frac{\partial^2\psi}{\partial v_f^2} \cdot W_{sf} = 0$ and $\frac{\partial^2\psi}{\partial v_f^2} \cdot V_{sf} = 0$ intersect on the line of the compound.

That this must really be so, is easily seen, when we bear in mind, that on the line of the compound the locus where $\frac{\partial^2\psi}{\partial v_f^2} = 0$ coincides with that where $\frac{\partial^2\psi}{\partial v_f^2} \cdot V_{sf} = 0$, from which in connection with equation (10) it follows immediately that at the same point also $\frac{\partial^2\psi}{\partial v_f^2} \cdot W_{sf} = 0$. In this way we arrive at the conclusion, that the three loci $\frac{\partial^2\psi}{\partial v_f^2} = 0$, $\frac{\partial^2\psi}{\partial v_f^2} \cdot V_{sf} = 0$ and $\frac{\partial^2\psi}{\partial v_f^2} \cdot W_{sf} = 0$ will intersect on the line

of the compound, and that therefore the loci $\frac{\partial^2\psi}{\partial v_f^2} \cdot V_{sf} = 0$ and $\frac{\partial^2\psi}{\partial v_f^2} \cdot W_{sf} = 0$ will interchange places on the left and the right of the line of the compound.

By means of equation (10) we understand now easily that the sign of the quantity $\frac{\partial^2\psi}{\partial v_f^2} \cdot W_{sf}$ must be negative outside the locus $\frac{\partial^2\psi}{\partial v_f^2} \cdot W_{sf} = 0$, and positive within it.

As connecting link for the transition to the P,T-lines we might discuss the V,T-lines; for this purpose we should then have to make use of the following equation (Cont. II, 106)

$$\left[(V_s - V_f)\frac{\partial^2\psi}{\partial v_f^2} + (x_s - x_f)\frac{\partial^2\psi}{\partial v_f \cdot \partial x_f}\right] dv_f + \left[(v_s - v_f)\frac{\partial^2\psi}{\partial v_f \cdot \partial x_f} + \right.$$
$$\left. + (x_s - x_f)\frac{\partial^2\psi}{\partial x_f^2}\right] dx_f = -(\varepsilon_{sf})_v \frac{dT}{T}.$$

By taking x constant we derive from this

$$T\left(\frac{dv_f}{dT}\right)_{x_f} = \frac{-(\varepsilon_{sf})_v}{(v_s - v_f)\frac{\partial^2\psi}{dv_f^2} + (x_s - x_f)\frac{\partial^2\psi}{\partial x_f \partial v_f}}.$$

or

$$T\left(\frac{dv}{dT}\right)_{x_f} = \frac{-(\varepsilon_{sf})_v}{\frac{\partial^2\psi}{\partial v_f^2} \cdot V_{sf}}.$$

I shall, however, not enter into a discussion of the VT-lines because it is to be seen even without this connecting link, what the course of the P,T-lines must be.

If now for simplication we call $\frac{\partial^2\psi}{\partial v_f^2} V_{sf} = X_1$ and $\frac{\partial^2\psi}{\partial v_f^2} \cdot W_{sf} = X_2$ and if we indicate what the signs are of these quantities in the different regions on the left and the right of the line of the compound, and where these quantities become $= 0$, we get the following:

left	*right*
$X_1 - X_2 -$ ..... $X_1 = 0$	$X_1 - X_2 -$ ..... $X_2 = 0$
$X_1 + X_2 -$ ..... $X_2 = 0$	$X_1 - X_2 +$ ..... $X_1 = 0$
$X_1 + X_2 +$ ..... $X_2 = 0$	$X_1 + X_2 +$ ..... $X_1 = 0$
$X_1 + X_2 -$ ..... $X_1 = 0$	$X_1 - X_2 +$ ..... $X_2 = 0$
$X_1 - X_2 -$	$X_1 - X_2 -$

If now led by equation

$$-T\left(\frac{dp}{dT}\right)_{x_f} = \frac{X_2}{X_1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

we draw the P, T-line for a concentration on the *left* of the curve of the compound, we obtain a curve as given by $GF'FD$ in fig. 2.

As we have assumed in our diagram, that the vapour-tension of A is the greatest and of B the smallest, whereas that of AB is intermediate, we cut now that branch of the three phase line of the compound, which has a maximum.

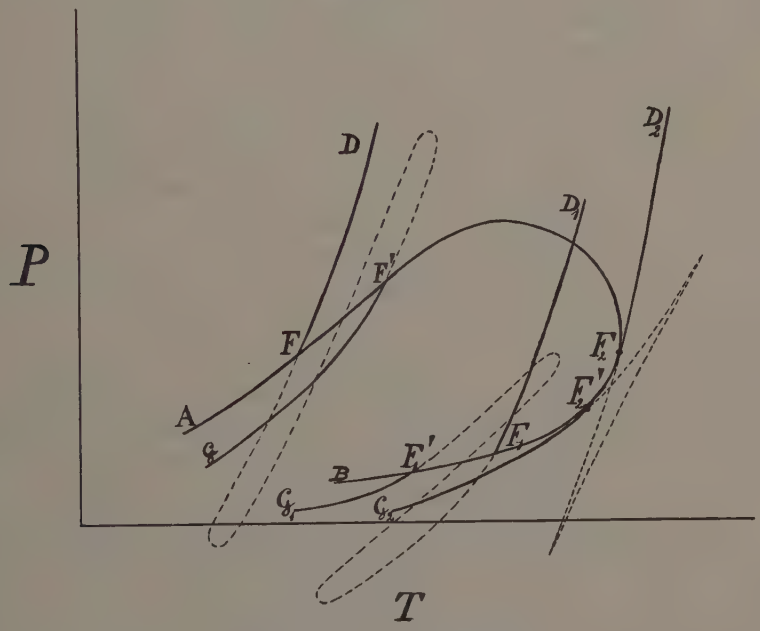


Fig. 2.

This intersection takes place in the points F' and F, about which it may be observed, that F'' lies at a higher temperature than F. This situation can, however, also be reversed, and as appears from the diagram, the transition takes place at a concentration somewhat to the left of that of the compound. We see further, that the intermediate piece, which continuously joins the line of sublimation GF' to the melting-point curve FD, has a maximum and a minimum (points where $X_2 = 0$), about which the isotherm teaches us, that, when we are not in the immediate neighbourhood of the critical state, they are very far apart and that the minimum lies at a negative pressure.

It is also noteworthy about this figure, that when following the P, T-line, starting with the point G resp. with the point D, we first meet with a point, where the tangent is vertical, and (place where $X_1 = 0$) *after that* with a point where it is horizontal.

If we now consider a concentration on the *right* of the line of the compound, the P, T-line corresponding with this will cut the other continually ascending branch of the three phase line of the compound, and by means of equation (4*a*) and the scheme for the reversal of sign of X_1 and X_2 preceding it, we obtain a curve as indicated by $G_1 F_1' F_1 D_1$. The situation of the loci $X_1 = 0$ and $X_2 = 0$ being different on the right from that on the left, this P, T-line differs from that just discussed. When now, starting from the point G_1 resp. D_1, we follow the P,T-line, we meet *first* with a point, where it is vertical, so we have just the reverse of the preceding case. About the situation of the points F_1' and F_1 we may point out, that F_1' *always* lies at lower temperature than F_1.

The loci $X_1 = 0$ and $X_2 = 0$ intersecting on the line of the compound, the P,T-line for the concentration of the compound will have to give to a certain extent the transition-case between the two lines discussed.

What happens when we approach the curve of the compound, we see immediately from fig. 1. The distance between the loci $X_1 = 0$ and $X_2 = 0$ becoming smaller and smaller, the points of contact of the vertical and horizontal tangents will draw nearer and nearer, which prepares us for what happens when we have arrived at the line of the compound. We see from the scheme for the signs of X_1 and X_2 that when the loci $X_1 = 0$ and $X_2 = 0$ have coincided, the signs of X_1 and X_2 reverse simultaneously, on account of which $T\left(\frac{dp}{dT}\right)_{x_f}$ retains the same sign, viz. remains positive. Combining this with what we know about the course of the P,T-lines somewhat to the right and the left of the curve of the compound we are led to the conclusion, that the P,T-line for the concentration of the compound will have two *cusps*, each formed by two branches with a common tangent. I have not been able to decide whether these points will be cusps of the first or the second kind. The former has been assumed in the diagram.

It is further noteworthy for this P,T-line that, as VAN DER WAALS [1]) already demonstrated before, both the line of sublimation and the melting-point line must touch the three-phase line, so that the P,T-line

[1]) Verslag 21 April 1897, 482.

for the concentration of the compound assumes a shape, as given by the line $G_2 F_2' F_2 D_2$ in fig. 2.

If it were possible to make the degree of association of the compound smaller and smaller, the points F_2' and F_2 would move to lower pressure and higher temperature. Moreover these two points and the neighbouring point of intersection of the melting-point and sublimation branches would draw nearer and nearer to each other, till with perfect absence of dissociation these *three* points would have coincided.

Another peculiarity will present itself for the case that we have a three-phase-line as described by me before, viz. with two maxima and one minimum [1]), for then there is a point where $x_d = x_l$ [2]) on

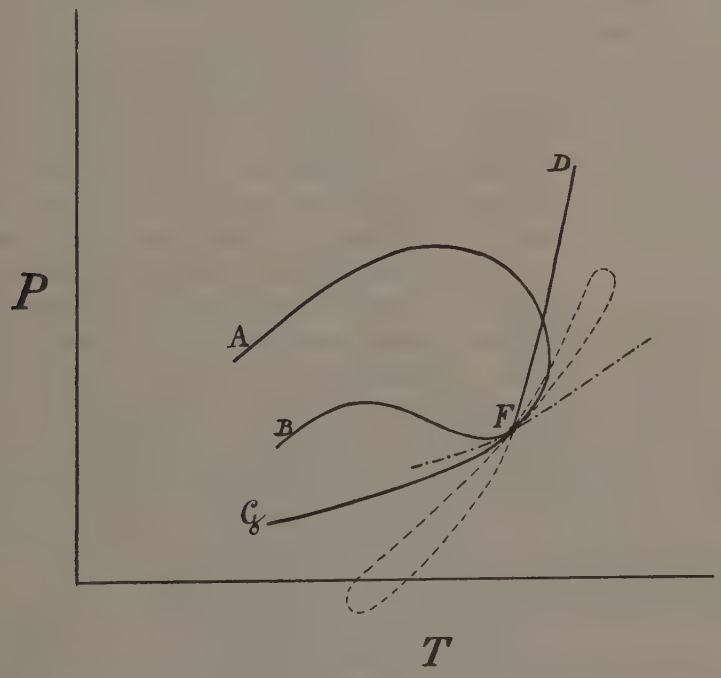


Fig. 3.

this line, and then it is immediately to be seen that in consequence of the coinciding of the points F' and F, we get for this concentration a P,T-line, as represented in fig. 3, which curve has the form of a *loop*.

Amsterdam, April 1906. *Anorg. Chem. Lab. of the University.*

[1]) These Proc. VIII, p. 200.

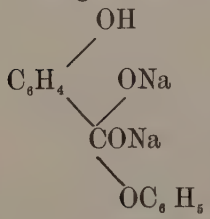
[2]) In this point the direction of the three-phase line is given by $T\frac{dp}{dT} = \frac{r}{v_d - v_l}$.

Chemistry. — *"The formation of salicylic acid from sodium phenolate."* By Dr. J. MOLL VAN CHARANTE. (Communicated by Prof. A. P. N. FRANCHIMONT).

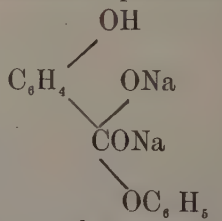
(Communicated in the meeting of April 27, 1906).

The communication from LOBRY DE BRUYN and TIJMSTRA read at the meeting of 28 May 1904 and their subsequent article in the Recueil **23** 385 induced me to make this research. Their theory, and particularly the proofs given in support do not satisfy me and as, in consequence of other work, I had formed an idea of the reaction I made some experiments in that direction.

According to my idea, an additive product of sodium phenolate with sodium phenylcarbonate, or what amounts to the same an additive product of two mols of sodium phenolate with one mol. of carbondioxide $C_6H_5OC(ONa)_2OC_6H_5$ might be the substance which undergoes the intramolecular transformation to the salicylic acid derivative and then forms, dependent on the temperature, sodium salicylate and sodium phenolate or else phenol and basic sodium salicylate. This view is supported by previous observations of various chemists and has been partially accepted also by CLAISEN [1]).



As LOBRY DE BRUYN and TIJMSTRA give no analytical figures in their paper it did not seem to me impossible that the phenolsodium-*o*-carboxylic acid obtained by them might be the substance formed by intramolecular transformation of my supposed additive product. I, therefore, took up their method of working, prepared sodium phenylcarbonate in the usual manner, from sodium phenolate and carbon dioxide, and heated this to 100° in a sealed tube for 100 hours. On opening the tube considerable pressure was observed. This pressure was always fonnd when the experiments were repeated. The gas liberated proved to consist entirely of carbondioxide and amounted to $^1/_4$—$^1/_3$ of that present in the sodium phenylcarbonate. If we argue that the sodium phenylcarbonate under these circumstances is partially resolved into carbon dioxide and sodium phenolate the latter compound ought to be present or else the splitting up might give carbon dioxide and my supposed

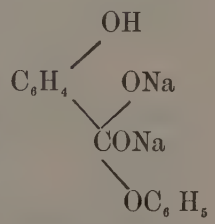


[1]) B. B. (1905) 38 p. 714.

intermediary product $(C_6H_5O)_2\,C(ONa)_2$. In the first case it is strange that during the cooling of the tube, which often was left for a few days, the carbon dioxide is not greatly reabsorbed. Those substances had now to be searched for in the product of the reaction. On treatment with ether a fair amount of phenol was extracted although moisture was as much as possible excluded. It was then brought into contact with cold, dry acetone, by which it was partially dissolved, but with evolution of gas and elevation of temperature. From the clear solution, petroleum ether precipitated a substance which, after having been redissolved and reprecipitated a few times in the same manner, formed small white needles containing acetone which effloresced on exposure to the air. On analysis, this compound proved to be sodium salicylate with one mol. of acetone. As an ebullioscopic determination in acetone, according to LANDSBERGER, did not give the expected molecular weight, sodium salicylate was dissolved in acetone and precipitated with petroleum ether and a quite identical product was obtained as proved both by analysis and determination of the molecular weight. Both products, after being dried at 100°, yielded no appreciable amount of salicylic ester when heated with methyl iodide.

The amount of sodium salicylate obtained by heating sodium phenylcarbonate in the manner indicated was, however, very trifling.

I suspected that the evolution of gas noticed in the treatment with acetone, and which was identified as pure carbondioxide without any admixture, was caused by the presence of unchanged sodium phenylcarbonate, so that, therefore, the reaction was not completed, and that the tube after being heated must still contain a mixture of unchanged sodium phenylcarbonate, sodium phenolate, sodium salicylate and free phenol, besides the said additive product $(C_6H_5O)_2$ $C(ONa)_2$ and the salicylic acid derivative possibly formed from this. I now thought it of great importance to first study the behaviour of acetone with these substances as far as they are known.



Sodium phenolate dissolves in boiling acetone, from which it crystallises on cooling in soft, almost white needles, several c.m. long, which contain one mol. of acetone. They lose this acetone, in vacuo, over sulphuric acid. At the ordinary temperature acetone dissolves only 0,1 %.

Sodium phenylcarbonate placed in carefully dried acetone gives off

carbon dioxide with a slight elevation of temperature. The quantity amounts to about $^1/_3$ of the carbon dioxide actually present, at least if account is taken of the comparatively large solubility of that gas in acetone. The acetone, or if the mixture is extracted with ether, also the ether, contains a quantity of phenol corresponding with the total amount obtainable from the sodium phenylcarbonate. The undissolved mass consists of a mixture of neutral and acid sodium carbonate, nearly, or exactly in equivalent proportions. The decomposition of 3 $C_6H_5OCOONa$ to 3 $C_6H_5OH + CO_2 + NaHCO_3 + Na_2CO_3$ requires 2 mols. of water. As the experiments however, have been made in a specially constructed apparatus into which no moisture or moist air could enter, with extremely carefully dried acetone, we are bound to admit that this water has been generated by the acetone, and we may, therefore, expect a condensation product of the acetone which, however, could not be isolated, owing to the small quantities of materials used in the experiments. It seems strange that in this reaction the evolution of carbon dioxide is so extraordinarily violent.

Sodium salicylate dissolves in acetone from which it crystallises, with or without addition of petroleum ether, in small needles, which may contain one mol. of acetone of crystallisation. In different determinations the acetone content was found to vary from one-half to a full molecule. At 16° it dissolves in about 21 parts of acetone.

Disodium salicylate was prepared by adding an (95%) alcoholic solution of salicylic acid to a concentrated solution of sodium ethoxide in alcohol of the same strength. After a few moments it crystallises in delicate, white needles. By boiling with acetone in which it is entirely insoluble it may be freed from admixed monosodium salicylate.

The behaviour of acetone with these substances now being known, the experiment of heating the sodium phenylcarbonate for 100 hours was once more repeated, without giving, however any further results. A portion was treated with acetone in the same apparatus which had been used for the sodium phenylcarbonate. A quantity of carbon dioxide was collected corresponding with an amount of unchanged sodium phenylcarbonate representing 50—60 % of the reaction-product. Another portion was extracted with ether and yielded about 20 % of phenol whilst, finally, a small amount of sodium salicylate was also found. The residue which had been extracted with ether and acetone contained sodium carbonate but no disodium-salicylate. It, however, contained phenol, probably from sodium phenolate.

It seems strange there is such a large quantity of free phenol

in the heated sodium phenylcarbonate, and as no disodium-salicylate has been found it cannot have been caused by the formation of that compound.

I have not been able to find the looked for additive product; perhaps it has been decomposed by acetone in the same manner as sodium phenylcarbonate. The results obtained show in my opinion that the formation of salicylic acid from sodium phenylcarbonate is not so simple as is generally imagined.

A more detailed account of research will appear in the "Recueil".

Chemistry. — "*On the crystal-forms of the* 2,4-*Dinitroaniline-derivatives, substituted in the* NH_2*-group*". By Dr. F. M. JAEGER. (Communicated by Prof. P. VAN ROMBURGH).

(Communicated in the meeting of April 27, 1906).

More than a year ago I made an investigation as to the form-relation of a series of position-isomeric *Dinitroaniline*-derivatives [1]). On that occasion it was shown how these substances exhibit, from a crystallonomic point of view, a remarkable analogy which reveals clearly the morphotropous influence of the hydrocarbon-residues, substituted in the NH_2-group.

Among the compounds then investigated, there were already a few 1-2-4-*Dinitroaniline*-derivatives kindly presented to me by Messrs. VAN ROMBURGH and FRANCHIMONT. Through the agency of Prof. VAN ROMBURGH and Dr. A. MULDER, I have now received a series of other derivatives of 2,4-*Dinitroaniline* which in the happiest manner complete my former publications. I wish to thank these gentlemen once more for their kindness. I will describe and illustrate all these derivatives in a more detailed article in the Zeits. f. Kryst.

For the present I will merely give a survey of the results obtained, which have been collected in the annexed table.

I have chosen such a form-symbolic, that the morphotropous relation of the great majority of these substances is clearly shown. They all possess the same family-character which is shown in the values of the axial relations and the topic parameters. Only a few of these substances show no simple relationship with the other ones.

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1) JAEGER, Ueber morphotropische Beziehungen bei den in der Amino-Gruppe substituierten Nitro-Anilinen; Zeits. f. Kryst. (1905). **40.** 113—146.

No.	Name of the compound	Survey			
		M.p.	Mol. weight.	Equiv. Vole. (in the solid state.)	
1	1-2-Nitro-Aniline.	72°	138	95.70	Rh
2	1-4-Nitro-Aniline.	146°	138	96.03	M
3	1-2-4-Dinitro-Aniline.	182°	183	113.30	M
4	1-2-4-6-Trinitro-Aniline.	190°	228	129.39	M
5	1-4-Nitro-Diethyl-A.*)	78°	194	162.07	M
6	1-2-4-Dinitro-Methyl-A.	178°	197	125.24	M
7	1-2-4-Dinitro-Ethyl-A.	114°	211	145.41	T
8	1-2-4-Dinitro-Dimethyl-A.	87°	211	142 95	Rh
9	1-2-4-6-Trinitro-Dimethyl-A.	154°	256	165.05	Rh
10	1-2-4-Dinitro-Methyl-Ethyl-A.	59°	225	157.45	T
11	1-2-4-Dinitro-Diethyl-A.	80°	239	173.94	Rh
12	1-2-4-, + 1-3-4-Dinitro-Diethyl-A. (Double compound.)	59°	478	½(361.02)	M
13	1-2-4-6-Trinitro-Diethyl-A.	164°	284	192.41	M
14	1-2-4-Dinitro-Ethyl-n-Propyl-A.	55°	253	189.13	Rh
15	1-2-4-6-Trinitro-Ethyl-Isopropyl-A.	109°	298	211.80	T
16	1-2-4-Dinitro-Isopropyl-A.	95°	225	153.79	T
17	1-2-4-Dinitro Dipropyl-A.	40°	267	202.50	R
18	1-2-4-6-Trinitro-Dipropyl-A.	138°	312	227.23	T
19	1-2-4-Dinitro-Isobutyl-A.	80°	239	172.70	M
20	1-2-4-6-Trinitro-Isobutyl-A	95°	284	196.53	R
21	1-2-4-Dinitro-Diisobutyl-A.	112°	295	250.21	D
22	1-2-4-Dinitro-Allyl-A.	76°	223	157.93	T
23	1-2-4-Dinitro-Methyl-Phenyl-A.	166°	273	194.16	D
24	1-2-4-Dinitro Ethyl-Phenyl-A.	95°	287	210.48	D
25	1-2-4-Dinitro-Benzyl-A.	116°	273	187.50	T
26	1-2-4-Dinitro-Methyl-Benzyl-A.	144°	287	204.41	D
27	1-2-4-Dinitro-Ethyl-Benzyl-A.	73°	301	219 87	
28	1-2-4-Dinitro-Phenyl-Benzyl-A.	168°	349	250.00	
29	1-2-4-6-Trinitro-Ethyl-Nitraniline.	96°	301	183.09	
30	1-2-4-6-Trinitro-Isopropyl-Nitraniline.	108°	315	201.53	
31	1-2-3-4-6-Tetranitro-Methyl-Nitraniline.	146°	332	189.71	

*) On the isomorphism and the complete miscibility of this compound with p-Nitrosodiethylanil

stallographically-investigated derivatives of 1—2—4—Dinitro-Aniline.

	Axial-Elements:	Topic Parameters:	No.
rr.	$a : b : c = 1.3667 : 1 : 1.1585.$	$\chi : \psi : \omega = 5.3635 : 3\ 9245 : 4.5465$	1
.	$a : b : c = 2.0350 : 1 : 1.4220;\ \beta = 88°10'$	$\chi : \psi : \omega = 6.5406 : 3.2141 : 4.5704$	2
.	$a : b : c = 1.9826 : 1 : 1\ 4088;\ \beta = 85°\ 1\frac{1}{2}'$	$\chi : \psi : \omega = 6.8206 : 3.4403 : 4.8467$	3
.	$a : b : c = 1.6560 : 1 : 1.5208;\ \beta = 80°47\frac{1}{2}'$	$\chi : \psi : \omega = 5.9313 : 3.8119 : 5.7975$	4
.	$a : b : c = 1.0342 : 1 : 0.9894;\ \beta = 80°34'$	$\chi : \psi : \omega = 5.6210 : 5.4351 : 5.3775$	5
.	$a : b : c = 1.2286 : 1 : 0.9707;\ \beta = 83°28'$	$\chi : \psi : \omega = 5.8090 : 4.7281 : 4.5897$	6
.	$a : b : c = 1\ 2251 : 1; 0.9745$ $\alpha = 33°25\frac{1}{2}'\ \ \beta = 83°22'\ \ \gamma = 75°41'.$	$\chi : \psi : \omega = 6.2321 : 5.0871 : 4.9880$	7
rr.	$a : b : c = 1.2154 : 1 : 1.0803.$	$\chi : \psi : \omega = 5.8035 : 4.7750 : 5.1583$	8
n.	$a : b : c = 1.2936 : 1 : 1.3831.$	$\chi : \psi : \omega = 5.8455 : 4.5184 : 6.2493$	9
.	$a : b : c = 1.1497 : 1 : 1.6639.$ $\alpha = 75°46'\ \ \beta = 92°33'\ \ \gamma = 68°57'$	$\chi : \psi : \omega = 5.1900 : 4.5140 : 7.5106$	10
r.	$a : b : c = 1.2045 : 1 : 1.1513.$	$\chi : \psi : \omega = 6.0294 : 5\ 0058 : 5.7631$	11
.	$a : b : c = 1.3435 : 1 : 1.3013;\ \beta = 86°39'$	$\chi : \psi : \omega = 6.3064 : 4.6940 : 6\ 1083$	12
.	$a : b : c = 1.1750 : 1 : 0\ 9462;\ \beta = 86°28'$	$\chi : \psi : \omega = 6.5523 : 5.5762 : 5.2763$	13
r.	$a : b : c = 1.0535 : 1 : 0.9227.$	$\chi : \psi : \omega = 6.1045 : 5.7946 : 5\ 3466$	14
.	$a : b : c = 2\ 0162 : 1.$ $\alpha = 75°0'\ \ \beta = 99°17'\ \ \gamma = 111°16\frac{1}{2}'$	———	15
.	$a : b : c = 1.1527 : 1 : 1\ 5790.$ $\alpha = 118°43'\ \ \beta = 104°33'\ \ \gamma = 85°12\frac{1}{2}'$	$\chi : \psi : \omega = 5.3440 : 4.6360 : 7.3201$	16
r.	$a : b : c = 1.0191 : 1 : 0.9246.$	$\chi : \psi : \omega = 6\ 1042 : 5.9890 : 6.5382$	17
.	$a : b : c = 1.3327 : 1 : 0\ 9055$ $\alpha = 119°46'\ \ \beta = 111°0'\ \ \gamma = 102°35'$	$\chi : \psi : \omega = 8.1556 : 6.1197 : 5.5414$	18
.	$a : b : c = 0.7104 : 1 : 0.3591;\ \beta = 85°34\frac{1}{2}'$	$\chi : \psi : \omega = 6.1870 : 8.7092 : 3.2145$	19
rr.	$a : b : c = 0.7325 : 1 : 0\ 3470.$	$\chi : \psi : \omega = 6.7231 : 9.1782 : 3.1849$	20
.	$a : b : c = 1.0717 : 1 : 0.9124;\ \beta = 63°5\frac{1}{2}'$	$\chi : \psi : \omega = 7.0686 : 6.5960 : 6.0181$	21
.	$a : b : c = 1.0251 : 1 : 0.9632$ $\alpha = 71°16\frac{1}{2}'\ \ \beta = 111°0'\ \ \gamma = 116°40'$	$\chi : \psi : \omega = 5.9480 : 5.8024 : 5.5890$	22
.	$a : b : c = 1.1518 : 1 : 1.6968;\ \beta = 86°1'$	$\chi : \psi : \omega = 5.3389 : 4.6341 : 7.8650$	23
.	$a : b : c = 0.4933 : 1 : 0.6586;\ \beta = 78°6\frac{1}{4}'$	$\chi : \psi : \omega = 4.2994 : 8.7156 : 5.7401$	24
.	$a : b : c = 1.0385\ \ 1 : 0.8586$ $\alpha = 107°57'\ \ \beta = 139°47'\ \ \gamma = 78°23'$	$\chi : \psi : \omega = 7.2441 : 6.9757 : 5.9891$	25
.	$a : b : c = 1.5086 : 1 : 1.3276;\ \beta = 71°40'$	$\chi : \psi : \omega = 7.1735 : 4.7551 : 6.3129$	26
.	$a : b : c = 1.7258 : 1 : 1.3087;\ \beta = 84°5'$	$\chi : \psi : \omega = 6.9531 : 4.6084 : 6.0310$	27
.	$a : b : c = 1.1373 : 1 : 1.3645;\ \beta = 64°21\frac{1}{2}'$	$\chi : \psi : \omega = 6.4059 : 5.7640 : 7.6856$	28
.	$a : b = 1.4187 : 1.\ \ \beta = 86°23\frac{1}{4}'$	———	29
.	$a : b : c = 1.3924 : 1 : 0.9968;\ \beta = 78°33'$	$\chi : \psi : \omega = 7.3676 : 5.2913 : 5.2743$	30
.	$a : b : c = 1.6686 : 1 : 1.4712;\ \beta = 76°37'$	$\chi : \psi : \omega = 7.1730 : 4.2987 : 6.3243$	31

se Proceedings (1905) p. 658.

Crystallography. — *"On a new case of form-analogy and miscibility of position-isomeric benzene-derivatives, and on the crystal-forms of the six Nitrodibromobenzenes."* By Dr. F. M. JAEGER. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated in the meeting of April 27, 1906).

§ 1. The following contains the investigation of the crystal-forms exhibited by the six position-isomeric *Nitrodibromobenzenes*, which may be expected from the usual structure-representations of benzene. It has been shown that, in this fully investigated series, there again exists a miscibility and a form-analogy between two of the six terms.

The above compounds were kindly presented to me by Prof. HOLLEMAN, to whom I again express my thanks.

This investigation is connected with that on the isomeric *Dichloronitrobenzenes*, which has also appeared in these proceedings (1905, p. 668).

A. Nitro-2-3-Dibromobenzene.

Structure: $C_6H_3 . (NO_2)_{(1)} . Br_{(2)} . Br_{(3)}$; meltingpoint: 53° C.

The compound, which is very soluble in most organic solvents,

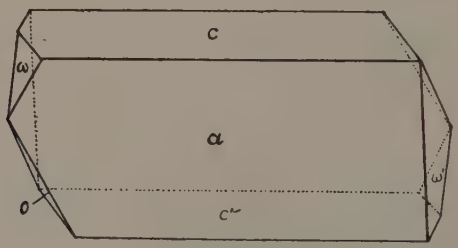

Fig. 1.

crystallises best from ligroïn + ether in small, flat, pale sherry-coloured needles which generally possess very rudimentary terminating planes.

Triclino-pinacoidal.

$$a : b : c = 1{,}4778 : 1 : 1{,}9513.$$

$A = 90°30'$	$\alpha = 90°45^1/_2'$
$B = 110°37'$	$\beta = 110°36^3/_4'$
$C = 90°16^1/_2'$	$\gamma = 89°59^1/_4'$

The crystals, therefore, show a decided approach to the monoclinic system; on account, however, of their optical orientation, they can only be credited with a triclinic symmetry.

The forms observed are: $a = \{100\}$, strongly predominant and very lustrous; $b = \{010\}$, smaller but yielding good reflexes; $c = \{001\}$, narrower than a, but very lustrous; $o = \{1\bar{1}\bar{1}\}$, well developed and very lustrous; $\omega = \{1\bar{1}1\}$, smaller but very distinct; $s = \{\bar{1}\bar{1}\bar{1}\}$, very narrow but readily measurable.

The habit is elongated towards the b-axis with flattening towards $\{100\}$.

	Measured:	*Calculated:*
$a : b = (100) : (0\bar{1}0) =$	* 90°16½'	—
$a : c = (100) : (001) =$	* 69 23	—
$a : o = (100) : (1\bar{1}\bar{1}) =$	* 65 11	
$c : o = (00\bar{1}) : (1\bar{1}\bar{1}) =$	* 75 47⅓	—
$b : o = (0\bar{1}0) : (1\bar{1}\bar{1}) =$	* 36 6	—
$a : \omega = (100) : (1\bar{1}1) =$	50 52	50°49'
$c : \omega = (001) : (1\bar{1}1) =$	56 52	56 43
$b : \omega = (0\bar{1}0) : (1\bar{1}1) =$	46 28	46 35
$o : \omega = (1\bar{1}\bar{1}) : (1\bar{1}1) =$	47 13	47 29⅓
$a : s = (\bar{1}00) : (\bar{1}1\bar{1}) =$	49 59	50 49⅓
$b : s = (0\bar{1}0) : (\bar{1}\bar{1}\bar{1}) =$	45 48	45 52½
$c : s = (00\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	—	56 4
$o : s = (1\bar{1}\bar{1}) : (\bar{1}\bar{1}\bar{1}) =$	63 39	63 59⅓

Readily cleavable, parallel $\{100\}$.

The extinction on $\{100\}$ amounts to about 26½ in regard to the b-axis; in convergent light a hyperbole is visible occupying an eccentric position.

The sp. gr. of the crystals is 2,305 at 8°; the equivalent volume 121.47.

B. Nitro-2-5-Dibromo-Benzene.

Structure: $C_6H_3 . (NO_2)_{(1)} . Br_{(2)} . Br_{(5)}$; m.p.: 84°,5.

This compound has been previously studied crystallographically by G. Fels, (Zeits. f. Kryst. **32**, 377). This paper, however, contains several errors, which render a renewed investigation desirable; moreover, another choice of axial (coordinate) planes is required, which makes the crystals show more analogy with the other triclinic terms of this series.

The crystals deposited from acetone + ligroïn have the form of small plates flattened towards $\{001\}$ (figs. 2 and 3). They are pale yellow and very lustrous.

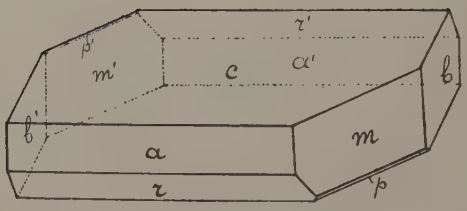

Fig. 2.

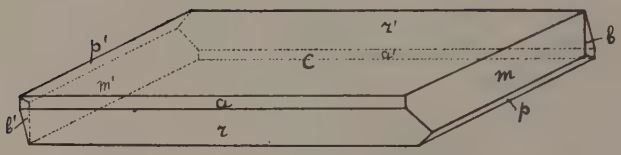

Fig. 3.

Triclino-pinacoïdal.

$$a : b : c = 1{,}4909 : 1 : 2{,}0214.$$

$A = 91° 3\frac{1}{2}'$	$\alpha = 90°57\frac{1}{2}'$
$B = 113°21\frac{1}{2}'$	$\beta = 113°21\frac{1}{2}'$
$C = 90°27'$	$\gamma = 90° 2'$.

Forms observed: $c = \{001\}$, strongly predominant and reflecting ideally; $a = \{100\}$, and $r = \{\bar{1}01\}$, usually developed equally broad and also yielding sharp reflexes; $b = \{010\}$, smaller, readily measurable; $m = \{110\}$, large and lustrous; $p = \{11\bar{3}\}$, mostly narrow but very lustrous; sometimes as broad as m.

Broad flattened towards $\{001\}$. The approach to monoclinic symmetry is also plain in this case.

	Measured:	*Calculated:*
$a : b = (100) : (010)$	$=$*89°33′	—
$b : c = (010) : (001)$	$=$*88 $56\frac{1}{2}$	—
$c : a = (001) : (100)$	$=$*66 $38\frac{1}{2}$	—
$b : m = (010) : (110)$	$=$*35 $59\frac{1}{2}$	—
$a : r = (100) : (10\bar{1})$	$=$*43 45	—
$c : m = (001) : (110)$	$= 75\ 46$	$75°38\frac{2}{3}'$
$a : m = (100) : (110)$	$= 53\ 33$	$53\ 33\frac{1}{2}$
$c : r = (00\bar{1}) : (10\bar{1})$	$= 69\ 37$	$69\ 36\frac{1}{2}$
$r : m = (10\bar{1}) : (110)$	$= 65\ 20$	$65\ 11$
$p : m = (11\bar{3}) : (110)$	$= 60\ 59$	$60\ 44\frac{1}{2}$
$r : b = (10\bar{1}) : (010)$	$= 89\ 55$	$89\ 22$
$r : p = (10\bar{1}) : (11\bar{3})$	$= 50\ 53$	—

Readily cleavable, parallel *m*.

The optical orientation is that of FELS, in which his forms {010}, {001} and {11$\bar{1}$} assume, respectively, in my project the symbols {001}, {110} and {010}. It may be remarked that FELS has incorrectly stated the structure and also the melting point. Moreover, his angles (11$\bar{1}$) : (100) and (11$\bar{1}$) : (010) appear to be $> 90°$. Perhaps it is owing to this, that the agreement between the calculated and found values is with him so much more unfavourable than with me. I have never observed forms {$\bar{5}$52} and {$\bar{1}\bar{5}$. 15 . $\bar{4}$}

The sp. gr. at 8° is 2,368; the equiv. volume: 118,66.

Topical axes: $\chi : \psi : \omega = 5{,}2190 : 3{,}5005 : 7{,}0758$.

On comparing the said position-isomeric derivatives, one notices at once not the great similarity between the two compounds, which, although constituting a case of direct-isomorphism, still very closely resembles it.

Nitro-2-3-*Dibromobenzene.*
Triclino-pinacoidal.

$a : b : c = 1{,}4778 : 1 : 1{,}9513$
$A = 90°30'$ $B = 110°37'$ $C = 90°16^1/_2'$
$\alpha = 90°45^2/_3'$ $\beta = 110°36^3/_4'$ $\gamma = 89°59^1/_4'$
$\chi : \psi : \omega = 5{,}2565 : 3{,}5571 : 6{,}9409$.

However:

Forms: {100}, {010}, {001}, {1$\bar{1}\bar{1}$}, {1$\bar{1}$1} and {$\bar{1}\bar{1}$1}

Cleavable parallel {100}.
Habit tabular towards {100}.

Nitro-2-5-*Dibromobenzene.*
Triclino-pinacoidal.

$a : b : c = 1{,}4909 : 1 : 2{,}0214$.
$A = 91°3^1/_2'$ $B = 113°21^1/_2'$ $C = 90°27'$
$\alpha = 90°57^1/_2'$ $\beta = 113°21^1/_3'$ $\gamma = 90°2'$
$\chi : \psi : \omega = 5{,}2190 : 3{,}5005 : 7{,}0758$.

However:

Forms: {100}, {010}, {001}, {$\bar{1}$01}, {110}, {11$\bar{3}$}.

Cleavable parallel {110}.
Habit tabular towards {001}.

We, therefore, still notice such a difference in habit and cleavability that a direct isomorphism, in the ordinary meaning of the word, cannot be supposed to be present. There occurs here a case of isomorphotropism bordering on isomorphism.

Notwithstanding that difference, both substances can form an interrupted series of mixed crystals, as has been proved by the determination of the binary melting point curve and also crystallographically [1]).

The melting point of the 1-2-3-derivative (53°) is depressed by addition of the 1-2-5-derivative. The melting point line has also

[1]) The binary melting-curve possesses, — as proved by means of more a exact determination, — a *eutectic point* of 52° C. at 2% of the higher melting component; therefore here the already published melting-diagram is eliminated. There is a *hiatus* in the series of mixed-crystals, from $\pm$ ½% to circa 48% of the 1-2-3-derivative. I shall, however point out, that the possibility of such a hiatus thermodynamically can be proved, — even in the case of directly-isomorphous substances.
(Added in the English translation).

not, as in the previously detected case of the two tribromotoluenes (Dissertation, Leyden 1903) a *continuous* form; the difference is caused by the lesser degree of form-analogy which these substances possess in proportion to that of the two said *tribromotoluenes*.

The third example of miscibility, — although partially —, and of form-analogy of position-isomeric benzene-derivatives [1]) is particularly interesting.

Mixed crystals were obtained by me from solutions of both components in acetone + ether.

They possess the form of fig. 1 and often exhibit the structure of a sand time-glass or they are formed of layers. With a larger quantity of the lower-melting derivative, long delicate needles were obtained which are not readily measurable. The melting points lie between ± 75° and 84½°; I will determine again more exactly the mixing limits.

C. Nitro-2-4-Dibromobenzene.

Structure: $C_6H_3 . (NO_2)_{(1)} . Br_{(2)} . Br_{(4)}$; m. p. 61°.6.

Recrystallised from alcohol, the compound forms large crystals flattened towards *a* and elongated towards the *c*-axis. They are of a sulphur colour.

Triclino-pinacoidal.

$$a : b : c = 1{,}1307 : 1 : 1{,}1698.$$

$A = 97°13\frac{1}{2}'$	$\alpha = 97°36'$
$B = 113°30\frac{1}{2}'$	$\beta = 113°37'$
$C = 90°38\frac{1}{2}'$	$\gamma = 87°33'$

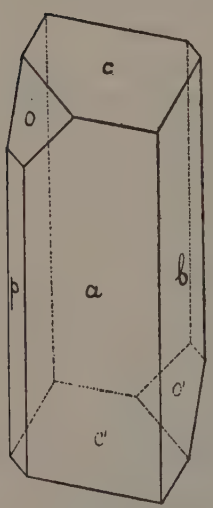

Fig. 4.

Forms observed: $a = \{100\}$ predominant and very lustrous; $b = \{010\}$ and $c = \{001\}$, equally broad, both strongly lustrous; $p = \{1\bar{1}0\}$, narrow but readily measurable; $o = \{1\bar{1}1\}$, large and yielding good reflexes.

The compound has been measured previously, by Groth and Bodewig (Berl. Berichte, **7**, 1563). My results agree in the main with theirs; in the symbols adopted here, their *a*- and *b*-axes have changed places and the agreement with the other derivatives of the series is more conspicuous.

[1]) The examples now known are 1-2-3-5-, and 1-2-4-6-*Tribromobenzene*; 1-2-3-5-*Tribromo*-4-6-*Dinitro*- and 1-2-4-6-*Tribromo*-3-5-*Dinitrotoluene*; and 1-2-5-, and 1-2-3-*Nitrodibromobenzene*, partially miscible.

	Measured:	*Calculated:*
$a : b = (100) : (010)$	$=$* 89°21½′	—
$a : c = (100) : (001)$	$=$* 66 29½′	—
$b : c = (010) : (001)$	$=$* 82 46½′	—
$p : a = (1\bar{1}0) : (100)$	$=$* 46 36	—
$c : o = (001) : (1\bar{1}1)$	$=$* 48 42	—
$o : p = (1\bar{1}1) : (1\bar{1}0)$	$=$ 51 43 (circa)	52° 1′
$c : p = (001) : (\bar{1}10)$	$=$ 100 29 (circa)	100 43′

Cleavable towards {010}; GROTH and BODEWIG did not find a distinct plane of cleavage.

Spec. Gr. of the crystals = 2,356, at 8° C., the equiv. vol. = 119,27.

Topic Axes: $\chi : \psi : \omega = 5{,}2365 : 4{,}6304 : 5{,}4166$.

Although the analogy of this isomer with the two other triclino-isomers is plainly visible, the value of $a : b$ is here quite different. In accordance with this, the derivative melting at 84½° *lowers* the melting point of this substance. A mixture of 87% 1-2-4- and 13% 1-2-5-*Nitrodibromobenzene* melted at 56°. There seems, however, to be no question of an isomorphotropous mixing.

D. Nitro-2-6-Dibromobenzene.

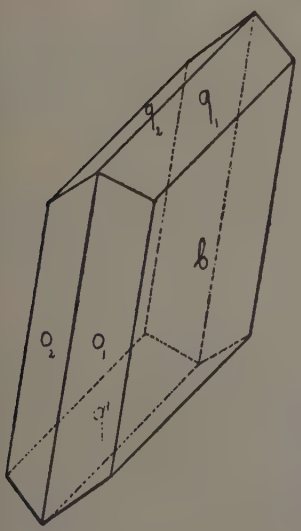

Fig. 5.

Structure: $C_6H_3(NO_2)_{(1)} . Br_{(2)} . Br_{(6)}$; m.p. 82°.

Recrystallised from alcohol the compound generally forms elongated, brittle needles which are often flattened towards two parallel planes.

Monoclino-prismatic.

$$a : b : c = 0{,}5678 : 1 : 0{,}6257.$$

$$\beta = 83°24'.$$

Forms observed: $b = \{010\}$, strongly predominant; $q = \{011\}$ and $o = \{111\}$ about equally strongly developed. The crystals are mostly flattened towards b with inclination towards the a-axis.

	Measured:	*Calculated:*
$q : q = (011) : (0\bar{1}1) =$	* 63°43½'	—
$o : o = (111) : (11\bar{1}) =$	* 47 52	—
$o : q = (111) : (0\bar{1}1) =$	* 74 20½	—
$o : q = (111) : (011) =$	45 42½	45°42'
$q : b = (011) : (010) =$	58 8¼	58 8¼
$b : o = (010) : (111) =$	66 6	66 4

No distinct plane of cleavage is present. An optical investigation was quite impossible owing to the opaqueness of the crystals.

Sp. Gr. = 2,211 at 8° C.; the equiv. vol.: 127,09.

Topic parameters: $\chi : \psi : \omega = 4{,}0397 : 7{,}1147 : 4{,}4516$.

E. Nitro-3-5-Dibromobenzene.

Structure: $C_6H_3(NO_2)_{(1)} . Br_{(3)} . Br_{(5)}$; m.p.: 104°,5. The compound has already been measured by Bodewig (Zeitschr. f. Kryst. **1**. 590); my measurements quite agree with his.

Monoclino-prismatic.

Bodewig finds $a : b : c = 0{,}5795 : 1 : 0{,}2839$, with $\beta = 56°12'$. Forms: {110}, {100}, {001} and {011}.

I take $\beta = 85°26'$ and after exchanging the *a*-, and *c*-axis

$$a : b : c = 0{,}5678 : 1 : 0{,}4831,$$

with the forms {011}, {001}, {201} and {211}. Completely cleavable towards {201}. Strong, negative double refraction.

Sp. Gr. = 2,363 at 8° C.; equiv. vol. = 118,91.

Topic axes: $\chi : \psi : \omega = 4{,}3018 : 7{,}5761 : 3{,}6601$.

The great analogy in the relation $a : b$ of this and of the previous substance is remarkable; also that of the value of angle β.

F. Nitro-3-4-Dibromo-Benzene.

Structure $C_6H_3(NO_2)_{(1)} . Br_{(3)} . Br_{(4)}$; m.p. 58° C. Has been measured by Groth and Bodewig (Berl. Ber. **7**.1563). *Monoclino-prismatic.*

$a : b = 0{,}5773 : 1$ with $\beta = 78°31'$. Forms {001}, {110} and {100}, tabular crystals. Completely cleavable towards {100}, distinctly so towards {010}. The optical axial plane is {010}; on *a* both optical axes (80°) are visible. I found the sp. gr. at 8° C. to be 2,354. The equivalent volume is therefore 119,34.

I have tried to find a meltingpoint-line of the already described type in the monoclinic derivatives in which some degree of form-analogy is noticeable. However, in none of the three binary mixtures this was the case; the lower melting point was *lowered* on addition of the component melting at the higher temperature, without formation of mixed crystals. For instance:

A mixture of 82,3% 1-2-3- and 17,7% 1-3-5-*Nitrodibromo-benzene* melted at 48½° C.

A mixture of 76,5% 1-2-6- and 23,5% 1-3-5-*Nitrodibromo-benzene* at 68½° C.

A mixture of 90,5% 1-3-4- and 9,5% 1-2-6-*Nitrodibromo-benzene* at 54° C.

Moreover, no mixed crystals could be obtained from mixed solutions.

The slight form-analogy with the *Nitro-dichloro-benzenes* [1]) investigated by me some time ago is rather remarkable.

Nitro-2-3-*Dichloro-Benzene* (62° C. rhombic) and *Nitro*-2-6-*Dichloro-Benzene* (71° C. monoclinic) exhibit practically no form-analogy with the two *Dibromo*-compounds. There is also nothing in the *Dichloro*-derivatives corresponding with the isomorphotropous mixture of the 2-3- and 2-5-*Dibromo*-product. The sole derivatives of both series which might lead to the idea of a direct isomorphous substitution of two *Cl*- by two *Br*-atoms are the *Nitro*-3-5-*Dihalogen-Benzenes* (65° C. and 104°,5 C.); the melting point of the *Dichloro*-derivative is indeed *elevated* by an addition of the *Dibromo*-derivative.

As a rule, the differences in the crystal-forms of the compounds of the brominated series are much less than those between the forms of the chlorinated derivatives — a fact closely connected with the much greater value which the molecular weight possesses in the *Nitro-Dibromo-Benzenes* than in the corresponding *Chloro*-derivatives.

Zaandam, April 1906.

Physiology. — "*On the nature of precipitin-reaction.*" By Prof. H. J. Hamburger and Prof. Svante Arrhenius (Stockholm).

(Communicated in the meeting of April 27, 1906).

One of the most remarkable facts discovered during the last years in the biological department, is most certainly the phenomenon that when alien substance is brought into the bloodvessels the individual reacts upon it with the forming of an antibody. By injecting a

1) These Proc. VII, p. 668.

toxin into the bloodvessels, the result is, that this is bound and free antitoxin proceeds. EHRLICH explains this as follows. When a toxin is injected, there are most probably cells which contain a group of atoms able to bind that alien substance. Now WEIGERT has stated the biological law, that when anywhere in the body tissue is destroyed, the gap usually is filled up with overcompensation. So, it may be assumed, that when the cell looses free groups of atoms, so many of these new ones are formed, that they can have no more place on this cell and now come in free state in circulation. This group of atoms is the antitoxin corresponding to the toxin.

As a special case of this general phenomenon the forming of precipitin is to be considered.

When a calf is repeatedly injected with horseserum, which can be regarded as a toxic liquid for the calf, then after some time it appears that in the bloodserum of that calf an antitoxin is present. In taking some bloodserum from this calf and by adding this to the horseserum a sediment proceeds. This sediment is nothing else than the compound of the toxin of the horseserum with the anti-toxin that had its origin in the body of the calf. We are accustomed to call this antitoxin *precipitin*, and the toxin here present in the horseserum, and which gave cause to the proceeding of precipitin, *precipitinogen* substance. The compound of both is called *precipitum*.

It is very remarkable that such a precipitate proceeds only, when the precipitin is brought in contact with its *own* precipitinogen substance. Indeed by adding the designed calfserum containing precipitin, not to the horseserum but to the serum of another animal, no precipitate proceeds. In this we have also an expedient to state if in a liquid (e.g. an extract of blood stain) horseserum is present or not (UHLENHUTH, WASSERMANN inter alia). Meanwhile such a calfserum gives notwithstanding also a precipitum with serum of the ass related to the horse.

To the same phenomenon the fact is to be brought, that when a rabbit has been injected with oxenserum, the serum taken from the rabbit does not only give a precipitate with oxenserum but also with that of the sheep and the goat, which are both related to the ox.

Some time ago an expedient was given to distinguish also [1]) serum proteid from *related* species of animals by a quantitative way, and in connection with this a method [2]) was proposed to determine accu-

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[1]) H. J. HAMBURGER, Eine Methode zur Differenzirung von Eiweiss biologisch verwandter Thierspecies. Deutsche Med. Wochenschr. 1905, S. 212.

[2]) H. J. HAMBURGER, Zur Untersuchung der quantitativen Verhältnisse bei der Präcipitinreaction. Folia haematologica. II Jahrg. N°. 8.

rately the quantity of precipitate which is formed by the precipitin reaction. This method also permitted to investigate quite generally the conditions which rule the formation of precipitate from the two components.

Immediately two facts had pushed themselves forward by a preliminary study which were also stated in another way by EISENBERG [1]) and ASCOLI [2]).

1. That when to a fixed quantity of calfserum [3]) (precipitin = antitoxin) increasing quantities of diluted horseserum (precipitinogen substance = toxin) were added, the quantity of precipitate increased, in order to decrease by further admixture of diluted horse serum.

2. that whatever may have been the proportion in which the two components were added to each other, the clear liquid delivered from precipitate always give a new precipitate with each of the components separately. This leads to the conclusion that here is question of an equilibrium reaction in the sense as it has been stated and explained for the first time by ARRHENIUS and MADSEN [4]).

This conclusion has become also the starting point of the now following researches of *which the purpose was to investigate by quantitative way the principal conditions by which precipitin reaction is ruled.*

Methods of investigation.

To a fixed quantity of calfserum [5]) (precipitin = antitoxin) increasing quantities of diluted horse-serum (precipitinogen substance =

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[1]) EISENBERG. Beiträge zur Kenntniss der specifischen Präcipitationsvorgänge Bulletin de l'Acad. d. Sciences de Cracovie. Class. d. Sciences Mathem. et nat. p. 289.

[2]) ASCOLI. Zur Kenntnis der Präcipitinewirkung. Münchener Med. Wochenschr. XLIX Jahrg. S. 398.

[3]) They used sera of other animals.

[4]) ARRHENIUS und MADSEN. Physical chemistry to toxins and antitoxins. Festskrift ved indvielsen of Statens Serum Institut. Kjobenhavn 1902; Zeitschr. f. physik. Chemie **44**, 1903, S. 7.

In many treatises the authors have continued these investigations; compare e.g. still:

ARRHENIUS. Die Anwendung der physikalischen Chemie auf die Serumtherapie. Vortrag gehalten im Kaiserl. Gesundheitsamt zu Berlin am 22 Sept. 1903. Arbeiten aus dem Kaiserl. Gesundheitsamt **20**, 1903.

ARRHENIUS. Die Anwend. der physik. Chemie auf die Serumtherapeutischen Fragen. Festschrift f. BOLTZMANN 1904. Leipzig, J. A. BARTH.

[5]) To make it easy for the reader, we speak here only of calfserum and horseserum. Compare the third note on this page.

toxin) are added. There upon the mixtures are heated for one hour at 37° and then centrifugated in funnelshaped tubes of which the capillary neck was fused at the bottom. The in 100 equal volumes calibrated capillary portion contains 0.02 or 0.04 c.c. The centrifugating is continued till the volume of the precipitate has become constant [1]).

Experiment with calf-horse serum.

As it was of importance, at all events for the first series of proofs, to dispose of a great quantity of serum containing precipitin, a large animal was taken to be injected. Dr. M. H. J. P. THOMASSEN at Utrecht was so kind to inject at the Governement Veterinaryschool there, a large calf several times with fresh horse serum and to prepare the serum out of the blood drawn under asceptic precautions.

The serum used for the following series of experiments was collected Nov. 28, 1905, sent to Groningen and there preserved in ice. On the day of the following experiment January 25, 1906, the liquid was still completely clear and free from lower organisms; there was only on the bottom a thin layer of sediment, which naturally was carefully left behind at the removing of the liquid. [2])

The horseserum used for the proof in question was fresh and 50 times diluted with a sterile NaCl-solution of 1%.

Each time two parallel proofs were taken as a control. The capillary portion of the funnel shaped tubes used for this experiment had a calibrated content of 0.04 cc. Each division of the tubes thus corresponded to 0.0004 cc.

To this series of experiments another was connected in which the quantity of diluted horseserum was constant, but increasing quantities of calfserum were used.

From the first table it appears, that when to 1 cc. calfserum increasing quantities of diluted horseserum are added, the quantity of precipitate rises. When more horseserum is added as is the case in the second table, the quantity of precipitate descends. This appears from the following.

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[1]) Compare Folia haematologica l. c. for further particulars of the method.

[2]) Fuller details of other proofs taken on other days with calf-horseserum, also of experiments with serum obtained by injecting rabbits with pig-, oxen-, sheep- and goat-serum will be communicated elsewhere.

TABLE I.

1 *cc of the mixture of* 1 *cc. calfserum* (precipitin or serum containing antitoxin) + ... cc. horseserum $^1/_{50}$ (precipitinogen or toxin containing serum.	Volume of the precipitate, after centrifugating for: ½ h. - ½ h. - ½ h. - ½ h. - ½ h. - 20m. - 15m.	The quantity of precipitate found in 1cc. of the mixtures calculated for the *total* quantity of the mixed components according to the last observation.
$\frac{0.04}{3}$ cc. horseserum $^1/_{50}$	1 — $^1/_2$ — not to be measured accurately	
$\frac{0.04}{3}$ » » »	1 — $^1/_2$ — » » » » »	
$\frac{0.08}{3}$ » » »	3 — 3 — 3 — 3 — 3 — 3 — 3	3.08
$\frac{0.08}{3}$ » » »	3 — 3 — 3 — 3 — 3 — 3 — 3	3.08
$\frac{0.1}{2}$ » » »	12 — 11 — 10 — 10 — 10 — 10 — 10	10.5
$\frac{0.1}{2}$ » » »	12 — 11 — 10 — 10 — 10 — 10 — 10	10.5
$\frac{0.16}{2}$ » » »	26 — 23 — 20 — 18 — 17 — 17 — 17	18.4
$\frac{0.16}{2}$ » » »	26 — 23 — 20 — 18 — 17 — 17 — 17	18.4
$\frac{0.2}{2}$ » » »	32 — 26 — 24 — 22 — 21 — 21 — 21	23.1
$\frac{0.2}{2}$ » » »	33 — 26 — 24 — 22 — 21 — 21 — 21	23.1
0.13 » » »	48 — 43 — 39 — 34 — 32 — 32 — 32	36.2
0.13 » » »	48 — 43 — 39 — 34 — 32 — 32 — 32	36.2
0.15 » » »	52 — 45 — 40 — 36 — 34 — 34 — 34	39.1
0.15 » » »	50 — 45 — 40 — 36 — 34 — 34 — 34	39.1
0.18 » » »	65 — 61 — 54 — 48 — 42 — 43 — 43	50.7
0.18 » » »	65 — 61 — 54 — 48 — 42 — 43 — 43	50.7
0.2 » » »	65 — 62 — 55 — 49 — 45 — 45 — 45	54
0.2 » » »	65 — 62 — 55 — 49 — 45 — 45 — 45	54
0.25 » » »	78 — 73 — 65 — 58 — 55 — 53 — 53	66.3
0.25 » » »	78 — 73 — 65 — 58 — 54 — 53 — 53	66.3
0.3 » » »	85 — 80 — 70 — 62 — 58 — 57 — 57	74.1
0.3 » » »	84 — 80 — 70 — 62 — 58 — 57 — 57	74.1

So e. g. the quantity of precipitate when 0.3 cc. horse serum is added to 1 cc. calfserum, is 74.1 (table I). But when, as may be read in the second table 0.5 cc. horse serum is added to 0.9 cc. calfserum the precipitate has a volume

TABLE II.

1 cc of the mixture of 0.5 cc horseserum $^1/_{50}$ + ... cc calfserum.	Volume of the precipitate, after centrifugating for ½ h. - ½ h. - ½ h. - ½ h. - ½ h. - 20m. - 15m.	The quantity of precipitate found in 1cc of the mixtures calculated for the total quantity of the mixed components, according to the last observation.
0.1 cc calfserum,	1 — ½ — not to be measured accurately	
0.1 » »	1 — ½ — » » » » »	
0.3 » »	2 — 2 — 2 — 2 — 2 — 2 — 2	1.6
0.3 » »	2 — 2 — 2 — 2 — 2 — 2 — 2	1.6
0.5 » »	6 — 5 — 5 — 5 — 5 — 5 — 5	5
0.5 » »	7 — 5 — 5 — 5 — 5 — 5 — 5	5
0.7 » »	48 — 36 — 32 — 28 — 25 — 25 — 25	30
0.7 » »	50 — 38 — 33 — 29 — 25 — 25 — 25	30
0.9 » »	84 — 65 — 57 — 50 — 43 — 43 — 43	51.6
0.9 » »	81 — 63 — 55 — 49 — 43 — 43 — 43	51.6
1.1 » »	95 — 81 — 67 — 58 — 52 — 50 — 50	80
1.1 » »	94 — 81 — 68 — 56 — 52 — 50 — 50	80
1.3 » »	92 — 79 — 66 — 59 — 59 — 55 — 55	99
1.3 » »	97 — 80 — 69 — 60 — 59 — 55 — 55	99
1.5 » »	96 — 84 — 74 — 65 — 62 — 59 — 59	118
1.5 » »	95 — 84 — 73 — 64 — 62 — 59 — 59	118
1.9 » »	90 — 75 — 65 — 55 — 53 — 51 — 51	122.4
1.9 » »	89 — 75 — 65 — 55 — 53 — 51 — 51	122.4

of 51.6. If instead of 0.9 calfserum 1 cc. was used the quantity of horseserum would necessarily have amounted to $0{,}5 \times \frac{1}{0\,9} = 0{,}55$ cc. So it appears that by the addition of 0.3 cc. horseserum to 1 cc. calfserum the precipitate amounts to 74.1 and by the addition of 0.55 cc. horseserum but to 37.3 [1]).

This decrease must be attributed partly to the solubility of the precipitum in NaCl-solution, a solubility which is felt the more strongly as a greater quantity of diluted horseserum is added. (Compare also Fol. Haematol l. c.).

So we see that the clear liquid above the precipitate contains, besides free precipitin and free precipitinogen substance, as has already been stated, also dissolved precipitate.

These three substances must form a variable equilibrium, which according to the rule of GULDBERG and WAAGE is to be expressed by the following relation.

Concentration of the free precipitinogen subst. × Concentr. of the precipitin = k_1 × Concentr. of the dissolved precipitate . . . . (I)

in this k_1 is the constant of reaction.

Meanwhile it appears from the experiment, that a greater quantity of precipitate must be dissolved than corresponds with this equation, or to express it more clearly, than corresponds with the conception that the solubility of the precipitate in NaCl solution is the only fact by which the quantity of sediment decreases.

To take away the difficulty, the hypothesis was made *that still another portion of the precipitate forms a dissolvable compound with free precipitinogen substance* (of horseserum) and that we have here a case analogical to the reaction of CaH_2O_2 with CO_2. As is known CaH_2O_2 is precipitated by CO_2, but by addition of more CO_2 the sediment of $CaCO_3$ decreases again, while CO_2 with $CaCO_3$ forms a dissolvable substance.

As will soon be seen, a very satisfactory conformity between calculated and observed quantity of precipitate is obtained through this hypothesis, which could afterwards be experimentally affirmed.

Let us now try, reckoning both with the solubility of the precipitate in NaCl-solution and with the forming of a dissolvable mixture of precipitate with precipitinogen substance, to precise more closely equation I.

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[1]) The hyperbolic form of the precipitate curve with ncreasing quantity of horseserum may still appear from the following series of experiments taken on another day (Table III). This series has not been used for the following calculation.

TABLE III.

1 cc of the mixture of 1 cc calfserum + ... cc horseserum $^1/_{50}$.	Volume of the precipitate after centrifugating for: ½ h. — ½ h. — ½ h. — ½ h. — 20 m. — 15 m. — 10 m.	The quantity of precipitate found in 1 cc. of the mixtures calculated for the *total* quantity of the mixed components according to the last observation.
0.1 cc horseser. $^1/_{50}$	38 — 38 — 28 — 24 — 23 — 23 — **23**	25.3
0.1 » » »	40 — 32 — 29 — 24 — 23 — 23 — **23**	25.3
0.2 » » »	66 — 54 — 48 — 44 — 42 — 42 — **42**	50.4
0.2 » » »	59 — 50 — 45 — 43 — 41 — 41 — **41**	50.4
0.3 » » »	88 — 69 — 65 — 56 — 55 — 55 — **55**	71.5
0.3 » » »	87 — 68 — 65 — 56 — 55 — 55 — **55**	71.5
0.4 » » »	98 — 76 — 70 — 62 — 58 — 57 — **57**	79.8
0.4 » » »	89 — 73 — 68 — 62 — 58 — 57 — **57**	79.8
0.6 » » »	84 — 62 — 57 — 49 — 44 — 44 — **44**	70.4
0.6 » » »	71 — 57 — 53 — 47 — 43 — 43 — **43**	68.8
0.7 » » »	65 — 49 — 45 — 39 — 37 — 37 — **37**	62.9
0.7 » » »	66 — 49 — 45 — 39 — 37 — 37 — **37**	62.9
0 8 » » »	61 — 45 — 40 — 38 — 33 — 31 — **31**	55.8
0.8 » » »	62 — 45 — 40 — 38 — 33 — 31 — **31**	55.8
0.9 » » »	41 — 30 — 26 — 25 — 22 — 21 — **21**	39.9
0.9 » » »	41 — 30 — 26 — 25 — 22 — 21 — **21**	39.9
1 » » »	24 — 17 — 15 — 15 — 13 — 13 — **13**	26
1 » » »	25 — 10 — 15 — 15 — 13 — 13 — **13**	26
1.2 » » »	2 — 2 — 2 — 2 — 2 — 2 — **2**	4
1.2 » » »	2 — 2 2 — 2 — 2 — 2 — **2**	4
1.4 » » »	not to be measured	
1.4 » » »	» » » »	

Firstly we shall try to find an expression for the three substances occurring in the clear liquid which stands above the precipitate: for the free precipitinogen substance, for the free precipitin which it contains and for the quantity of dissolved precipitate.

Firstly the quantity of *free precipitinogen substance*. Let A be the *total* quantity of that substance used for an experiment. To determine how much of this is still present in the liquid in free state, it is to be determined how much is bound. Bound is:

1. a certain quantum to form the precipitate which is present in solid condition. If we set down as a rule that 1 mol. precipitum proceeds from 1 mol. precipitinogen substance and 1 mol. precipitin, then the wanted precipitinogen substance will be expressed by P, if the molecular quantity precipitate also amounts to P.

2. a quantity pV when p represents the percentage of the quantity of dissolved precipitate and V the total volume of the liquid.

3. a quantity necessary to form the compound of precipitate- and precipitinogen substance. Admitting that 1 mol. of this compound proceeds from 1 mol. precipitate and 1 mol. precipitinogen substance and then that y of this compound is present, then together $2y$ must be charged, while in each of the two components y mol. precipitinogen substance is present, so that the quantity of precipitinogen substance, which is left in free state, amounts to

$$A-P-pV-2y.$$

So when the volume of the liquid is V, the *concentration* of the free precipitinogen substance =

$$\frac{A-P-pV-2y}{V} \quad \ldots\ldots\ldots \quad (2)$$

It is possible to calculate in the same way the concentration of the free precipitin.

If B is the *total* quantity of precipitin, which is used for the experiment, then there is to be subtracted from this:

1st. a quantity P for the same reason as is given at the calculation of the free precipitinogen substance (see above).

2nd. a quantity pV, likewise as explained there.

3rd. a quantity necessary to form the compound precipitate-precipitinogen substance. While in this compound but 1 mol. precipitin is present, only $1y$ is to be charged. So that the quantity of precipitin which remains in free state, amounts to $B-P-pV-y$.

While the volume of the liquid amounts to V, the concentration of the free precipitin is =

$$\frac{B-P-pV-y}{V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

As for the *concentration* of *dissolved precipitate* in the third place, this must be expressed by

$$\frac{pV}{V} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

So the equation (1) becomes:

$$\frac{A-P-pV-2y}{V} \times \frac{B-P-pV-y}{V} = k_1 \frac{pV}{V}$$

or

$$\mathbf{(A-P-pV-2y)\,(B-P-pV-y) = k_1\,pV^2} \quad . \quad . \quad . \quad (5)$$

Now one more equation, expressing the reaction according to which precipitate combines with precipitinogen substance. This is to be written down as follows.

Concentration free precipitinogen substance $\times$ concentr. dissolved precipitate $=$ k_2 concentr. compound precipitinogen subst. — precipitate.

$$\frac{A-P-pV-2y}{V} \times \frac{pV}{V} = k_2 \frac{y}{V}$$

or

$$\mathbf{(A-P-pV-2y)\,p = k_2\,y} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

By putting shortly $P+pV = P'$ and by substituting the value of y of equation (6) into equation (5) we obtain

$$\left(A-P'-2p\frac{A-P'}{k_2+2p}\right)\left(B-P'-p\frac{A-P_1}{k_2+2p}\right) = k_1\,pV^2 \quad . \quad . \quad (7)$$

In this equation are known:

1st. A, the total quantity of precipitinogen substance (diluted horseserum added);

2nd. B, the total quantity of precipitin (calfserum) used;

3rd. V, the volume of the liquid resulting from the mixing of the two components;

4th. P, the quantity of solid precipitate directly observed.

Unknown are:

1st. p, the quantity in percentages of precipitate which is *dissolved* (so p represents the solubility of the precipitate);

2nd. k_1, the constant for reaction of the formation of precipitate;

3rd. k_2, the constant for reaction of the formation of the compound precipitate-precipitinogen substance;

4th. P', this is however $P+pV$ and therefore known as soon as p has become known.

As equation (7) contains 3 unknown quantities three observations will be necessary to determine them.

When we introduce then the so found values in the other experiments and calculating the quantity of precipitate, it appears that the calculated quantities correspond in very satisfactory way with those which are observed.

Let us observe that to avoid superfluous zeros 1 cc calfserum (B) is taken $= 100$.

While as appears from the experiments in the case in question 1 cc calfserum is equivalent to nearly $^1/_3$ cc horseserum 1 : 50, 1 cc horseserum 1 : 50, that is A, obtains a value of 300.

So, where in the first experiment $\frac{0{,}04}{3}$ cc. horse serum was used A obtains a value of $\frac{0{,}04}{3} \times 300 = 4$.

In the experiment, where on 1 cc. calfserum 0,3 cc. horseserum was used, with a value $B = 100$, A becomes $0{,}3 \times 300 = 90$.

Let us now combine the two tables to one by calculating for the second table how much $^1/_{50}$ horseserum is used on 1 *calfserum*..

We see that the comformity between the determined and calculated precipitate (col. III and IV) is very satisfactory. The average of the discrepancy amounts to 1.3.

This result deserves our attention not only in view of the knowledge of the precipitin reaction as such, but also from a more general point of view, this reaction belonging to the great group of the toxin-antitoxin reactions.

Till now, in studying the last, we were obliged to deduce the equilibrium conditions from the toxins, that is to say by determining the toxic action which was left by the gradual saturation of the toxin by increasing quantities of antitoxin, but with the precipitin-reaction the equilibrium conditions may be deduced from the quantity of the formed toxin-antitoxin compound.

And not only that, but owing to the fact that the compound forms a precipitum, the quantity of this may be fixed in an accurate and direct way by simple measurement, thus without the aid of red blood corpuscles or of injecting-experiments in animals.

So there is good reason to expect that a further study of the precipitin-reaction will facilitate too the insight in other toxin-antitoxin reactions.

TABLE IV.

I	II	III	IV	V
1cc. calfserum, B = 100.				
Used quantity of horseserum $^1/_{50}$ (*on 1cc. calfserum*).	Used quantity of horseserum expressed in the just accepted units A.	*Determined* volumes of the precipitate in 1 cc. of the mixtures.	*Calculated* volumes of the precipitate in 1 cc. of the mixtures.	Difference between III and IV.
0.013 cc.	4	not to be measured.	0.2	
0.027 »	8	3	3.9	+ 0.9
0.05 »	15	10	10.3	+ 0.3
0.08 »	24	17	17.8	+ 0.8
0.1 »	30	21	23.6	+ 2.6
0.13 »	39	32	29.7	— 2.3
0.15 »	45	34	34	0
0.18 »	54	43	40.1	— 2.9
0.2 »	60	45	43.9	— 1.1
0.25 »	75 $\left\{\begin{matrix}53\\51\end{matrix}\right.$	52	52.1	— 0.1
0.266 »	79	51	53.6	+ 2.6
0.294 »	88.3	55	57.1	+ 2.1
0.3 »	90	57	57.5	+ 0.5
0.33 »	100	59	58.9	— 0.1
0.385 »	115.4	55	57.4	+ 2.4
0.457 »	137	50	51.3	+ 1.3
0 557 »	167	43	41.3	— 1.7
0.713 »	214	25	26.8	+ 1.8
1 »	300	5	5.5	+ 0.5
1.67 »	500	2	0	— 2

RÉSUMÉ.

We may resume our results as follows.

By mixing precipitin and precipitinogen substance (to compare resp. with antitoxin and toxin) an equilibrium reaction proceeds

obeying to the law of GULDBERG and WAAGE. By this equilibrium reaction part of the precipitin molecules combines with the corresponding quantity of molecules precipitinogen substance, while by the side of this compound a certain quantity of each of the two components remains in free state. The compound is partly precipitated and partly remains dissolved. How much remains dissolved depends for the greater part on the salt solution which is present, for the sediment is soluble in Na Cl-solution.

Besides this equilibrium reaction there is still another which consists in this, that part of the precipitate combines with free precipitinogen substance to a soluble compound. This reaction too obeys the law of GULDBERG and WAAGE. The case is to be compared with the precipitation of $Ca(OH)_2$ by CO_2. By excess of CO_2 a part of the resulting $CaCO_3$ is transformed in a soluble bicarbonate. So CaH_2O_2 takes the function of the precipitin and CO_2 that of the precipitinogen substance.

Astronomy. — "*Observations of the total solar eclipse of August* 30, 1905 *at Tortosa* (*Spain*)." By J. STEIN S.J. (Communicated by Prof. H. G. VAN DE SANDE BAKHUYZEN.)

At the invitation of Mr. R. CIRERA S. J., director of the new "Observatorio del Ebro" I went to Tortosa towards the end of June 1905 in order to take part in the observation of the total solar eclipse. I was charged with making the measurements of the common chords of the sun and moon at the beginning and at the end of the eclipse and had also to determine the moments of the four contacts. The results might perhaps contribute to the correction of the relative places of the sun and moon.

The determination of the co-ordinates was much facilitated by the circumstance that the signals of the three points Espina, Gordo and Montsià of the Spanish triangulation were visible at this place. The measurements of the angles with a theodolite yielded the following results:

$$\varphi = 40°49'\ 13''.43 \quad ; \quad \lambda = 1^m\ 58^s\ 18 \text{ east of Greenwich.}$$

In these results the spheroïdal shape of the earth is accurately taken into account. Later measurements made by Mr. J. UBAGH gave the same results. Electric time-signals, directly telegraphed from the Madrid observatory, gave for the longitude: $1^m\ 58^s.8$ east of Greenwich. As the most probable value we have adopted $1^m\ 58^s.5$,

the mean value of the two determinations. As a test 30 other determinations of latitude have been made with an instrument temporarily adjusted for Talcott observations, from which I derived as mean value: $\varphi = 40°49'\,14''.8$. The height above the sea-level is 55 meters.

The instrument at my disposal for the eclipse observation was a new equatorial of MAILHAT (Paris), $2^m.40$ focal length and 16 cm. aperture, provided with an eye-piece with a double micrometer. I have determined the screw value of one of the two screws from 18 transits of circumpolar stars near the meridian. I found for it:

$$R_1 = 60''.3534 \quad \pm 0''.0117;$$

the value of the other screw was determined by measuring the intervals by means of the first:

$$R_2 = 1.00010 \,.\, R_1.$$

The observatory possesses a good sidereal clock, the rate of which had been carefully determined during four months by means of star transits. In the night of 29—30 August, Mr. B. BERLOTY, a clever observer had observed 20 clock-stars, so that the accuracy of the determination of the clock-error left nothing to be desired.

During the phase observations the object-glass was reduced to 25 mm. by means of a screen of pasteboard. The eye-piece with a power of 30 was provided with a blue glass. The observations of the chords were continued as long as was allowed by the field of view of the eye-piece, which was more than 20′ in diameter. At my signal "top" the moments of the observations were noted by Mr. BELDA, who was seated in front of a mean time standard clock, which before, during, and after, the observations was compared with the sidereal clock; another assistant recorded the micrometer readings.

During the beginning and the end of the eclipse the sky in the neighbourhood of the sun was perfectly clear, so that I could perform the measurements of the chords undisturbed, although now and then I met with difficulties owing to irregularities in the rate of the driving clock. From some minutes before, until after, totality the sun was covered with light clouds, yet the moments of contact could be recorded with sufficient accuracy.

In the derivation of the results I have taken the solar parallax $= 8''.80$; for the rest I have borrowed the constants from the publication "Observatorio Astronomico de Madrid. Memoria sobre el eclipse total de Sol del dia 30 de Agosto de 1905". They are:

Mean radius of the sun $R_0 = 15'59''.63$ (AUWERS)
„ „ „ „ moon $r_0 = 15'32''.83$ (KUESTNER and BATTERMANN)
Parallax of the moon $\pi_0 = 57'\ 2''.68$

OBSERVATIONS.

First contact: 11 h 55 m 39 s .1 (mean time of Greenwich.)

	Length of the chords (corrected for refraction)
	"
11 h 56 m 28 s .2	294.93
57 12 .1	390.24
57 35 .2	437 22
58 20 .0	507.74
59 8 .2	566.98
59 38 .9	608.94
12 0 9 .2	642.58
1 25 .0	721.69
2 49 .9	798.82
4 18 .3	876.43
4 57 .0	906.12
5 44 3	935.04
6 15 .9	959.75
6 53 .2	983.94
7 18 .9	1004.93
8 1 .2	1030 37
8 43 .3	1052.50
9 23 .3	1078.17
9 49 .1	1096.89
10 16 .1	1106.16
10 42 .2	1124.37
11 9 .3	1138.90
11 26 .1	1144.49
11 56 .3	1160.37
12 24 .3	1178 82

Second contact: 1 h 16 m 13 s .2

Third contact: 1 19 7 .2

	Length of the chords
h m s	"
2 15 53 .0	1297.92

	Length of the chords
h m s	"
2 17 17 .3	1256 94
18 4 .5	1232.27
18 25 .3	1219.81
18 42 .5	1209.51
19 13 .3	1193.25
19 38 .2	1181.49
20 45 .0	1157.42
21 5 .3	1129.77
21 28 .3	1117.78
22 1 .0	1095.75
22 35 .3	1073.82
23 4 .1	1054.40
23 21 .3	1041.52
23 54 .3	1020.90
24 36 .0	993.28
25 2 .2	973.01
25 35 .3	950.47
26 2 .3	920.28
26 29 .3	903.24
26 52 .3	880 81
27 13 .3	863.90
27 36 .2	845.41
28 7 .6	819 14
28 43 .3	779.01
29 5 .3	762.98
29 38 .6	726.38
30 2 .3	697.40
30 22 .3	677.17
30 52 .3	637.13
31 14 .8	610.37
31 40 .6	573.84
32 4 .5	538.62
32 42 .6	480 78
33 3. .3	437.21
33 13 .3	406.92

Fourth contact: h m s 2 34 44 .7.

Right ascension of the sun, Aug. 30, 12^h M.T. Gr. $\alpha_\odot = 158°10'44''.24$
Declination „ „ „ „ „ „ $\delta_\odot = 9°\ 9'33''.19$
Right ascension of the moon „ „ „ „ $\alpha_(= 157°42'47''.95$
(HANSEN-NEWCOMB).
Declination „ „ „ „ „ „ $\delta_(= 9°53'\ 3''.48$
(HANSEN-NEWCOMB).

Each observation gives an equation of condition for the determination of the corrections Δ of the elements of the sun and moon. Let these corrections be successively

$$\Delta R,\ \Delta r,\ \Delta\alpha_\odot,\ \Delta\alpha_(,\ \Delta\delta_\odot,\ \Delta\delta_(,\ \Delta\pi,$$

then we obtain by comparing the observed distances and chords with those computed the following equations: (the coefficients have been rounded off to two decimals).

EQUATIONS OF THE CHORDS.

I. Observations after the first contact.

												Obs.—Comp.
					$\Delta\alpha$ (−⊙)		$\Delta\delta$ (−⊙)					" "
+7.98	ΔR	+7.97	Δr	+7.14	$\Delta\alpha$	−3.20	$\Delta\delta$	+1.67	$\Delta\pi$	=	+50.71	−10.36
+5.50	„	+5.49	„	+4.88	„	−2.19	„	+1.12	„		+36.23	− 5.57
+4.88	„	+4.87	„	+4.30	„	−1.93	„	+1.01	„		+37.59	+ 0.70
+4.10	„	+4.09	„	+3.56	„	−1.60	„	+0.81	„		+32.40	+ 1.78
+3.58	„	+3.57	„	+3.10	„	−1.39	„	+0.69	„		+22.49	− 2.13
+3.34	„	+3.32	„	+2.87	„	−1.29	„	+0.64	„		+24.96	+ 0.27
+3.15	„	+3.13	„	+2.69	„	−1.20	„	+0.59	„		+22.45	− 0.67
+2.78	„	+2.76	„	+2.34	„	−1.05	„	+0.51	„		+19.66	− 0.49
+2.50	„	+2.48	„	+2.06	„	−0.92	„	+0.43	„		+16.66	− 1.12
+2.29	„	+2.26	„	+1.85	„	−0.82	„	+0.38	„		+20.03	+ 4.06
+2.21	„	+2.18	„	+1.76	„	−0.79	„	+0.36	„		+19.60	+ 4.28
+2.13	„	+2.10	„	+1.68	„	−0.75	„	+0.34	„		+13.42	− 1.19
+2.08	„	+2.05	„	+1.63	„	−0.73	„	+0.33	„		+15.60	+ 1.43
+2.02	„	+1.99	„	+1.57	„	−0.70	„	+0.31	„		+14.57	+ 0.47
+1.99	„	+1.95	„	+1.53	„	−0.69	„	+0.30	„		+17.85	+ 4.46
+1.94	„	+1.90	„	+1.48	„	−0.66	„	+0.29	„		+15.73	+ 2.82
+1.89	„	+1.85	„	+1.43	„	−0.64	„	+0.27	„		+11.49	− 0.97
+1.85	„	+1.81	„	+1.38	„	−0.62	„	+0.26	„		+12.97	+ 0.87
+1.82	„	+1.78	„	+1.35	„	−0.60	„	+0.25	„		+16.44	+ 4.68
+1.80	„	+1.76	„	+1.32	„	−0.59	„	+0.25	„		+10.08	− 1.56
+1.77	„	+1.73	„	+1.30	„	−0 58	„	+0.24	„		+13.51	+ 1.19
+1.75	„	+1.71	„	+1.27	„	−0.57	„	+0.24	„		+12.97	+ 1.77
+1.74	„	+1.69	„	+1.26	„	−0.56	„	+0.23	„		+ 9.37	− 1.70
+1.71	„	+1.67	„	+1.23	„	−0.55	„	+0.22	„		+10.37	− 0.50
+1.69	„	+1.65	„	+1.21	„	−0.54	„	+0.22	„		+12.71	+ 2.06

II. Observations before the last contact.

												Obs.—Comp.	
												″	″
+1.52	ΔR	+1.46	Δr	−0.99	$\Delta\alpha$ (−⊙)	+0.49	$\Delta\delta$ (−⊙)	+0.16	$\Delta\pi$	=		− 5.39	+ 0.51
+1.57	„	+1.51	„	−1.05	„	+0.52	„	+0.18	„			− 5.30	+ 0.97
+1.60	„	+1.55	„	−1.09	„	+0.53	„	+0.19	„			− 5.84	+ 0.67
+1.61	„	+1.56	„	−1.10	„	+0.54	„	+0.19	„			− 7.39	− 0.76
+1.62	„	+1.57	„	−1.12	„	+0.55	„	+0.19	„			− 8.59	− 1.88
+1.64	„	+1.59	„	−1.14	„	+0.56	„	+0.20	„			− 8.19	− 1.31
+1.66	„	+1.62	„	−1.16	„	+0.57	„	+0.20	„			− 6.20	+ 0.81
+1.71	„	+1.67	„	−1.23	„	+0.59	„	+0.22	„			[+ 7.95]	—
+1.74	„	+1.70	„	−1.25	„	+0.61	„	+0.22	„			− 2.58	+ 4.99
+1.75	„	+1.71	„	−1.27	„	+0.62	„	+0.23	„			− 5.97	+ 1.72
+1.78	„	+1.74	„	−1.30	„	+0.64	„	+0.24	„			− 7.71	+ 0.22
+1.82	„	+1.78	„	−1.34	„	+0.66	„	+0.25	„			− 7.88	+ 0.29
+1.85	„	+1.81	„	−1.38	„	+0.67	„	+0.25	„			− 8.47	− 0.07
+1.87	„	+1.83	„	−1.40	„	+0.68	„	+0.26	„			− 9.75	− 1.22
+1.91	„	+1.87	„	−1.44	„	+0.70	„	+0.27	„			− 8.05	+ 0.78
+1.96	„	+1.93	„	−1.50	„	+0.73	„	+0.28	„			− 6.19	+ 3.02
+2.00	„	+1.97	„	−1.54	„	+0.75	„	+0.29	„			− 7.13	+ 2.15
+2.05	„	+2.02	„	−1.60	„	+0.78	„	+0.31	„			− 4.88	+ 4.94
+2.10	„	+2.07	„	−1.64	„	+0.80	„	+0.32	„			−13.04	− 2.92
+2.14	„	+2.12	„	−1.69	„	+0.82	„	+0.33	„			− 9.47	+ 0.96
+2.19	„	+2.16	„	−1.74	„	+0.85	„	+0.34	„			−12.56	− 1.80
+2.24	„	+2.21	„	−1.79	„	+0.87	„	+0.35	„			−11.04	+ 0.04
+2.29	„	+2.26	„	−1.84	„	+0.89	„	+0.36	„			−10.50	+ 0.87
+2.36	„	+2.34	„	−1.91	„	+0.93	„	+0.38	„			− 8.40	+ 3.46
+2.46	„	+2.44	„	−2.01	„	+0.98	„	+0.40	„			−14.81	− 2.31
+2.53	„	+2.51	„	−2.08	„	+1.01	„	+0.42	„			− 9.40	+ 3.53
+2.65	„	+2.63	„	−2.20	„	+1.06	„	+0.44	„			−11.28	+ 2.38
+2.74	„	+2.72	„	−2.29	„	+1.11	„	+0.46	„			−14.62	− 0.37
+2.83	„	+2.81	„	−2.37	„	+1.15	„	+0.48	„			−12.33	+ 2.47
+2.98	„	+2.96	„	−2.52	„	+1.22	„	+0.52	„			−16.88	− 1.15
+3.12	„	+3.10	„	−2.65	„	+1.28	„	+0.55	„			−15.37	+ 1.38
+3.29	„	+3.27	„	−2.81	„	+1.36	„	+0.58	„			−18.89	− 1.29
+3.49	„	+3.48	„	−3.00	„	+1.45	„	+0.63	„			−19.50	− 1.52
+3.90	„	+3.89	„	−3.39	„	+1.64	„	+0.71	„			−18.51	+ 2.74
+4.20	„	+4.19	„	−3.67	„	+1.77	„	+0.78	„			−26.71	− 3.86
+4.37	„	+4.34	„	−3.82	„	+1.85	„	+0.81	„			−38.87	−10.28

Equations of the contacts

$I \quad \Delta R + \Delta r + 0.903\ \Delta\alpha_{(-\odot)} - 0.405\ \Delta\delta_{(-\odot)} = +\ 3''.78$

$II \quad \Delta R - \Delta r - 0.9668\ \Delta\alpha_{(-\odot)} - 0.2007\ \Delta\delta_{(-\odot)} +$
$+ 0.0004\ \Delta^2\alpha_{(-\odot)} - 0.0036\ \Delta\alpha\Delta\delta + 0.0091\ \Delta^2\delta_{(-\odot)} = -\ 6''.52$ [1])

$III \quad \Delta R - \Delta r + 0.3085\ \Delta\alpha_{(-\odot)} - 0.9489\ \Delta\delta_{(-\odot)} +$
$+ 0.0104\ \Delta^2\alpha_{(-\odot)} + 0.0068\ \Delta\alpha\Delta\delta + 0.0012\ \Delta^2\delta_{(-\odot)} = +\ 4''.02$

$IV \quad \Delta R + \Delta r - 0.889\ \Delta\alpha_{(-\odot)} + 0.435\ \Delta\delta_{(-\odot)} = -\ 11''.18.$

A mere glance at the equations derived from the distances of the chords shows the impossibility to derive from them all the unknown quantities. On account of the proportionality of the coefficients we may use one single equation instead of the first 25 equations after the 1st contact; the same for the 35 others. In order to diminish the weight of the observations immediately after the first and before the last contact — when the chord is less sharply defined and varies rapidly — I have formed the two normal equations not according to the method of least squares but simply by addition.

We obtain the following equations:

$68.1(\Delta R+\Delta r)+56.2\Delta\alpha-25.2\Delta\delta=+489''.46 - 0.35(\Delta R-\Delta r) - 12.9\Delta\pi$
$-81.6(\Delta R+\Delta r)+65.1\Delta\alpha-31.6\Delta\delta=+397''.87+0.24(\Delta R-\Delta r)+12.8\Delta\pi$

whence:

$$\Delta R + \Delta r = +\ 1''.05 \ - 0.015\ \Delta\delta - 0.003\ (\Delta R - \Delta r) - 0.16\ \Delta\pi.$$
$$\Delta\alpha = +\ 7''.428 + 0.465\ \Delta\delta - 0.001\ (\Delta R - \Delta r) - 0.02\ \Delta\pi.$$

Neglecting the last terms, we find for the result from the equations derived from the length of the chords:

$$\Delta R + \Delta r = +\ 1''.05 \ - 0.015\ \Delta\delta_{(-\odot)}$$
$$\Delta\alpha_{(-\odot)} = +\ 7''.428 + 0.465\ \Delta\delta_{(-\odot)}.$$

From the equations of the 2nd and 3rd contact we derive:

$$\Delta\alpha_{(-\odot)} = +\ 7''.793 + 0.464\ \Delta\delta_{(-\odot)}.$$
$$\Delta\alpha_{(-\odot)} = +\ 7''.13 + 0.667\ (\Delta R - \Delta r)$$
$$\Delta\delta_{(-\odot)} = -\ 1''.43 + 1.437\ (\Delta R - \Delta r).$$

And lastly the equations of the 1st and 4th contact yield:

$$\Delta\alpha_{(-\odot)} = +\ 8''.35 + 0''.468\ \Delta\delta_{(-\odot)}$$
$$[\Delta R + \Delta r = -\ 3''.78]$$

The latter result for $\Delta R + \Delta r$, which differs entirely from that found above is little reliable. We can entirely account for it by assuming that the first contact has been observed too late and the last contact too early. It can hardly be doubted that the 1st contact

[1]) It is not allowed (as it is generally done) to neglect the quadratic terms in the equations of the 2nd and 3rd contact, because the corrections $\Delta\alpha$ and $\Delta\delta$, as compared with the distance between the centre of the sun and that of the moon, (in this case 46″) are too large.

is recorded too late because the eclipse began earlier than was expected and in consequence took me by surprise. As an evidence that the time of last contact was given too late there is an instantaneous photograph of the sun (diameter = 10 cm.) taken at the very moment when I gave the signal "top". This plate shows a small impression on the limb of the sun.

To enable me to compare the obtained results, Messrs. Th. Wulf and J. D. Lucas kindly put at my disposal the results of their highly interesting observations of the 2nd and the 3rd contact, made at Tortosa by means of sensitive selenium elements. (See for this Astron. Nachr. N°. 4071). They found:

beginning of totality $1^h\,16^m\,15^s,6$
end „ „ 1 19 6 ,9,

which yield the following equations:

$$\left.\begin{aligned} \Delta R - \Delta r - 0.9650\,\Delta\alpha_{(-\odot} - 0.2117\,\Delta\delta_{(-\odot} + 0.0004\,\Delta^2\alpha_{(-\odot} - \\ - 0.0039\,\Delta\alpha\,\Delta\delta + 0.0092\,\Delta^2\delta_{(-\odot} = -5''.73 \\ \Delta R - \Delta r + 0.3063\,\Delta\alpha_{(-\odot} - 0.9493\,\Delta\delta_{(-\odot} + 0.0105\,\Delta^2\alpha_{(-\odot} + \\ + 0.0069\,\Delta\alpha\,\Delta\delta + 0.0012\,\Delta^2\delta_{(-\odot} = +4''.10 \end{aligned}\right\} \quad (A)$$

whence

$$\Delta\alpha_{(-\odot} = +6''.42 + 0.653\,(\Delta R - \Delta r)$$
$$\Delta\delta_{(-\odot} = -1''.76 + 1.404\,(\Delta R - \Delta r).$$

When we subtract the two equations A from each other we get:

$$\Delta\alpha_{(-\odot} = +7''.238 + 0.465\,\Delta\delta_{(-\odot},$$

which agrees exceedingly well with the result of the chord equations $\Delta\alpha = +7''.428 + 0.465\,\Delta\delta$; but it also appears that it is impossible to determine $\Delta\alpha$, $\Delta\delta$ and $\Delta R - \Delta r$ separately from the combination of the contact and chord equations.

In the derivation of the final result we have accorded the same weight = 1 to the results of the chord measurements and to those of the contact determinations made by Wulf—Lucas, and the weight $\frac{1}{2}$ to my observations of the 2nd and 3rd contact. Thus we find, leaving out of account the first and the fourth contact:

$$\Delta R + \Delta r = +1''.07 - 0.02\,(\Delta R - \Delta r)$$
$$\Delta\alpha_{(-\odot} = +6''.66 + 0.66\,(\Delta R - \Delta r)$$
$$\Delta\delta_{(-\odot} = -1''.65 + 1.42\,(\Delta R - \Delta r).$$

The last column of the chord equations contains the deviations in the sense of observation — computation, which remain when we substitute these numerical values. The mean error of the first 25 observations (excluding the first) amounts to $\pm$ 2.″53; that of the last 35 (excluding the last) is $\pm$ 2.″21.

Chemistry. — "*On the osmotic pressure of solutions of non-electrolytes, in connection with the deviations from the laws of ideal gases.*" By J. J. VAN LAAR. (Communicated by Prof. H. W. BAKHUIS ROOZEBOOM.)

Communicated in the meeting of April 27, 1906).

1. By H. N. MORSE and J. C. W. FRAZER [1]) very accurate experiments were recently made on the determination of the osmotic pressure of *dilute* sugar solutions in water. The solutions had a concentration up to 1-normal, and as c is then about $^1/_{34}$ [the association factor of the water is viz. at 18° C. about 1,65, so that in 1 L. of water about $55{,}6 : 1{,}65 = 34$ Gr.mol. of water (simple and complex molecules) are present], the difference between the exact expression $-log(1-x)$ and the approximate value x [formula (2)] is not yet appreciable. It is however not so with the difference between the molecular volume of the *solution* $v = (1-x)\,v_1 + xv_2$ (v supposed to be a linear function of x, about which more presently) and the molecular volume of the *solvent* v_1, when v_2 (the molecular volume of the dissolved sugar) cannot be put equal to v_1. We shall see that this difference for 1-normal solutions amounts to $19\,^0/_0$, so that by means of the experiments we can very well ascertain, if we have to make use of v or of v_1. And these have really taught us, that the osmotic pressures measured agree (and even with very great accuracy) with the calculated values, *only* when v_1 is put in the numerator, and not v. This harmonizes therefore perfectly with what I have repeatedly asserted since 1894 [2]). (What I have called above v_1 for the sake of symmetry, was formerly always indicated by v_0). *Not* the molecular volume therefore of the whole solution, but the *molecular* volume of the *solvent in* the solution. And this deprives those of their last support, who in spite of all evidence (for not the dissolved substance, but the *solvent* brings about that pressure) persist in trying to explain the osmotic pressure by a pressure of the molecules of the dissolved substance comparable with the *gas pressure*. If such a thing could be thought of, v should be taken into consideration and not v_1, for the molecules of the dissolved substance move in the *whole* volume v and not in the volume v_1, which is perfectly fictitious with regard

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1) Amer. Chem. Journ. **34**, 1905, p. 1—99. See also the extensive abstract N° 274 in the Phys. Chem. Centralblatt III (1906).

2) See inter alia my previous paper on this subject in These Proceedings, May 27, 1905, p. 49. (Some remarks on Dr. PH. KOHNSTAMM's last papers).

to the *solution*, which would be equal to v only when v_2 happened to be equal to v_1.

2. In order to compare the results, found by MORSE and FRAZER, more closely with those for the osmotic pressure already given by me in 1894, we shall return to its derivation for a moment, chiefly in order to ascertain on what limiting suppositions this formula holds.

With equilibrium between the pure solvent (concentration 0, pressure p_0) and the *solvent* in the solution (concentration c, pressure p) [the dissolved substance is nowhere in equilibrium, for it is supposed that there is a membrane impenetrable to it] the molecular thermodynamic potentials must have the same value. Hence [1]):

$$\mu_1 (x, p) = \mu_1 (0, p_0) .$$

Now in general:

$$\mu_1 = \frac{\partial Z}{\partial n_1} = C_1 - \theta_1 + RT \log c_1 ,$$

when $C_1 = - k_1 T \ (\log T - 1) + ((e_1)_0 - T(s_1)_0)$, $c_1 = \frac{n_1}{\Sigma n_1}$ and $\theta_1 = \frac{\partial \Theta}{\partial n_1}$; Θ being given by

$$\Theta = \int p dv - pv - RT \Sigma n_1 . \log \Sigma n_1 .$$

For *binary* mixtures of *normal* substances we may now introduce the variable x and we obtain (Σn_1 is now $= 1$, so that the term with $\log \Sigma n_1$ vanishes), as may be supposed as known:

$$\mu_1 = C_1 - \left(\omega - x \frac{\partial \omega}{\partial x}\right) + p \left(v - x \frac{\partial v}{\partial x}\right) + RT \log (1 - x) , \quad . \quad (1)$$

when ω is written for $\int p dv$ by way of abbreviation.

This expression is *perfectly accurate* for the above mentioned mixtures. For the further calculation we now introduce the idea "*ideal*" mixtures. They are such as for which the *influence* of the two components *inter se* may be neglected. Then $\frac{\partial^2 \omega}{\partial x^2} = 0$, and ω becomes a *linear* function of x. But also $\frac{\partial^2 v}{\partial x^2} = 0$, so that v becomes

[1]) The following derivation is only different in form from the cited one in these Proceedings.

also a linear function of x. We shall further demonstrate this in § 6, and show that in the case of such mixtures:

$$\left\{\begin{array}{ll} a. & \omega \text{ is a linear function of } x \\ b. & v \quad ,, \quad ,, \quad ,, \quad ,, \quad ,, \quad ,, \\ c. & \dfrac{a}{b} \quad ,, \quad ,, \quad ,, \quad ,, \quad ,, \quad ,, \\ d. & \text{the heat of mixing is} = 0, \end{array}\right.$$

so that we may say: ideal mixtures are such *for which the heat of mixing is practically* $= 0$, or *with which no appreciable contraction of volume takes place*, when $1 - x$ Gr.mol. of one component is mixed with x Gr.mol. of the second.

The conditions a, b, c and d are *simultaneously* fulfilled, when the *critical pressures* of the two components are by approximation of the *same* value.

3. For $\omega - x\dfrac{\partial\omega}{\partial x}$ we may now write ω_1, as $\omega = (1 - x)\,\omega_1 + x\,\omega_2$, when $\dfrac{\partial^2\omega}{\partial x^2} = 0$. $\left[\text{Otherwise evidently } \omega - x\dfrac{\partial\omega}{\partial x} = \omega_1 - {}^1/_2 x^2\left(\dfrac{\partial^2\omega}{\partial x^2}\right)_1 - {}^1/_3\, x^3\left(\dfrac{\partial^3\omega}{\partial x^3}\right)_1 - \ldots\right]$ In the same way $v - x\dfrac{\partial v}{\partial x} = v_1$, and we get:

$$\left.\begin{array}{l} \mu_1(x, p) = C_1 - \omega_1 + pv_1 + RT\,log\,(1 - x) \\ \mu_1(o, p_0) = C_1 - \omega_1 + p_0 v_1 \end{array}\right\},$$

always when v_1 and ω_1 are supposed to be *independent* of the *pressure*. For else ω_1 and v_1 would have another value at the pressure p than at the pressure p_0. We must therefore also suppose that our liquids are *incompressible*. But there is not the slightest objection to this supposition for ordinary liquids far from the critical temperature (and there is only question of such liquids in discussions on the osmotic pressure). Only when x draws near to 1, and so the osmotic pressure would approach to ∞, v_1 (and so also ω_1) must no longer be supposed to be independent of p.

By equating these two last equations, we get:

$$pv_1 + RT\,log\,(1 - x) = p_0 v_1,$$

hence

$$\pi = p - p_0 = \frac{RT}{v_1}(-\log(1-x)) \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the expression already derived by me in 1894. [1])

[1]) Cf. Z. f. Ph. Ch. **15**, 1894; Arch. Teyler 1898; Lehrbuch der math. Chemie, 1901; Arch. Teyler 1903; Chem. Weekbl. 1905, N°. 9; These Proceedings, June 21, 1905.

In the original Dutch paper another note followed, which Mr. VAN LAAR has replaced by the following in the English translation.

A conversation with Dr. KOHNSTAMM suggested the following observations to me. Dr. KOHNSTAMM finds (These Proceedings, May 27, 1905) the quantity $v - x\frac{db}{dx}$ in the denominator of the expression for π. This is quite correct, and harmonizes perfectly with the general expression, which according to equation (1) on p. 54, would also have been found by me for non-linear variability of v.

Then we should viz. have:

$$p\left(v - x\frac{\partial v}{\partial x}\right)_p - p_0(v_1)_{p_0} = -RT\log(1-x) + \left(\omega - x\frac{\partial \omega}{\partial x}\right)_p - (\omega_1)_{p_0},$$

where, when calculating $\omega - x\frac{\partial \omega}{\partial x}$ by means of VAN DER WAALS' equation of state, also a term $-px\frac{\partial(v-b)}{\partial x}$ appears, in consequence of which $p\left(v - x\frac{db}{dx}\right)$ occurs in the first member.

Now it is of no importance whether v is diminished by $x\frac{\partial v}{\partial x}$ or by $x\frac{db}{dx}$, as $p\frac{\partial(v-b)}{\partial x}$ approaches to 0 both for small and for very large values of p. I therefore obtained a correction term in the denominator, *in connection with the size of the molecules* of exactly the same value as Dr. KOHNSTAMM. That this did not always clearly appear in my previous papers, is due to the fact that I then always introduced the approximation $v - x\frac{\partial v}{\partial x} = v_1$, which was perfectly justifiable for my purpose.

For as $v - x\frac{\partial v}{\partial x} = v_1 - {}^1/_2\, x^2\left(\frac{\partial^2 v}{\partial x^2}\right)_1 -$ etc., this is sufficiently accurate for practical purposes. (for ideal mixtures, where v is a linear function of x, it is of course *quite* accurate).

Yet in a so early paper as the one cited by K. of 1894 (Z. f. Ph. Ch. **15**, p. 464) it is clearly to be seen that the result obtained by me agrees perfectly with his. For it says (line 4 from the top) that $v_{a'}$ (the index a' is there always used for the liquid phase) $= \frac{\partial v}{\partial n_{a'}}$. But this is in the x-notation nothing but $v - x\frac{\partial v}{\partial x}$, the physical meaning of which is: the molecular volume of the water in the solution with the concentration x.

The phrase occurring on page 466: "und niemals etwa $v_{a'} - b$ im Sinne etc." refers there to the well-known attempts of EWAN and others. The same is the case with the phrase in the paper on non-diluted solutions in the Ch. Weekblad of June 7th 1905: "Ook heeft men getracht, etc." (p. 5).

We repeat once more: this expression holds from $x=0$ to $x=$ near 1, when the following conditions are satisfied:

a. the solution is an *ideal binary* mixture of *normal* components;

b. the solution is practically *incompressible.*

Then (2) represents the *additional pressure* on the *solution*, in order to repel the penetrating water (the so-called "*osmotic*" pressure).

As however in all the experiments made up to now *water* was the solvent, hence an *anomalous* substance, (2) must not be applied to solutions in water without reservation. It is, however, easy to show that the influence of the association does not play a part before the term with x^2 (just as the influence of the two components inter se), so that in the above experiments, where x^2 may undoubtedly be neglected (cf. § 1), formula (2) may certainly be used.

Let us, however, first reduce it to a form more practical for use.

4. Let us write (2) for this purpose:

$$\pi = \frac{RT}{v_1}(x + {}^1/_2\, x^2 + \ldots) = \frac{RT}{v_1}\, x\,(1 + \tfrac{1}{2}\, x), \quad . \quad . \quad . \quad (2a)$$

which is more than sufficient for solutions up to 1-normal. Let us further assume that c Gr. mol. are dissolved in 1000 Gr. H_2O (called by MORSE and FRAZER "weight-normal solutions"), then:

$$x = \frac{c}{34 + c} = \frac{c'}{1 + c'},$$

when we put ${}^1/_{34}\, c = c'$ ($34 = 55{,}6 : 1{,}65$ is the number of Gr. mol. H_2O in 1000 Gr. at 18° C; cf. § 1).

We find then:

$$\pi = \frac{RT}{v_1}\frac{c'}{1 + c'}\left(1 + {}^1/_2\,\frac{c'}{1 + c'}\right),$$

or when we restrict ourselves to terms of the second degree with respect to c':

$$\pi = \frac{RT}{v_1}\, c'\,(1 - {}^1/_2\, c') = \frac{RT}{v_1}\,\frac{c}{34}\,(1 - {}^1/_{68}\, c).$$

In this $R = 82{,}13$ (c.c.M., Atm.), and $v_1 = 1001{,}4 : 34$ cM³ at 18°. For $\dfrac{RT}{34\, v_1}$ we therefore find at 18° C.:

$$\frac{RT}{34 v_1} = \frac{82{,}13 \times 291{,}04}{1001{,}4} = 23{,}87,$$

hence

$$\pi_{18°} = 23{,}87\, c\,(1 - 0{,}015\, c) \text{ Atm.} \quad . \quad . \quad . \quad . \quad (2b)$$

We see from the calculation, as we already observed above, that

the influence of the association of the solvent is only appreciable in the term with c^2. If water were a normal liquid, we should have had $^1/_{111}\ c$ instead of $^1/_{68}\ c = 0{,}015\ c$. ($\frac{1}{2}\ c'$ would then be $= {}^1/_2 \times {}^1/_{55{,}6}\ c$).

Let us now consider what the last expression would have become for $\pi_{18°}$, when not v_1 had occurred in the denominator, but the molecular volume of the solution v.

When c Gr. mol. are dissolved in 1000 Gr. H_2O, then the total volume will be (at 18°) $1001{,}4 + 190\ c$ ccM. [For 1 Gr. mol. $= 342{,}2$ Gr. of melted sugar occupies a volume of 190 ccM. at 18° (density $= 1{,}8$)].

Altogether there are now $34 + c$ Gr. mol., hence the molecular volume of the solution will be:

$$v = \frac{1001{,}4 + 190\ c}{34 + c} = \frac{1001{,}4}{34}\ \frac{1 + 0{,}19\ c}{1 + 0{,}03\ c}.$$

For v_1 we found however above:

$$v_1 = \frac{1001{,}4}{34},$$

so that the value of $\pi_{18°}$ with v in the denominator instead of v_1 would have become:

$$\pi_{18°} = 23{,}87\ c\,(1 - 0{,}015\ c) \times \frac{1 + 0{,}03\ c}{1 + 0{,}19\ c}\ \text{Atm.},$$

i. e.

$$\pi_{18°} = 23{,}87\ c\ \frac{1 + 0{,}015\ c}{1 + 0{,}19\ c}\ \text{Atm.}$$

For (weight)normal solutions ($c = 1$) we should therefore have found instead of $\pi_{18°} = 23{,}87\ (1 - 0{,}015) = \underline{23{,}51}$ Atm., $\pi_{18°}$ $= 23{,}87 \times \frac{1{,}015}{1{,}19} = \underline{20{,}36}$ Atm.

Now Morse and Frazer found 24,52 Atm., which is considerably nearer the theoretical value 23,51 Atm. (with v_1 in the denominator) than near the inaccurate expression with v in the denominator [1]).

So it is out of the question that the molecules of the dissolved substance should exert a certain pressure comparable with the gas-pressure, for then the volume of the *solution as such*, viz. v, would have to be taken into account, and not the in that solution perfectly fictitious molecular volume of the solvent v_1.

5. But there is more. We shall viz. derive the expression for the pressure which *would* be exerted by the dissolved molecules,

[1]) With 0,5-normal the two values would have been 11,85 and 10,98 Atm., whereas 12,08 Atm. has been found experimentally.

when they, according to the inaccurate interpretation of the osmotic pressure, could move free and undisturbed throughout the space of the solution.

VAN DER WAALS' equation of state, viz.

$$p = \frac{RT}{v-b} - \frac{a}{v^2}$$

gives for the rarefied gas-state:

$$p = \frac{RT}{v}\left[\frac{v}{v-b} - \frac{a:RT}{v}\right] = \frac{RT}{v}\left(1 + \frac{b}{v} - \frac{a:RT}{v}\right),$$

when we again content ourselves with terms of the degree $\frac{1}{v^2}$.

Let us now write:

$$\frac{a}{RT} - b = \gamma,$$

then

$$p = \frac{RT}{v}\left(1 - \frac{\gamma}{v}\right),$$

where v now represents the volume, in which 1 Gr. mol. of the *dissolved substance* moves. This volume is however evidently (cf. also § 4):

$$v = \frac{1001{,}4 + 190\,c}{c},$$

or

$$v = \frac{1001{,}4}{c}(1 + 0{,}19\,c),$$

so that we get:

$$p = \frac{RT\,c}{1001{,}4\,(1 + 0{,}19\,c)}\left(1 - \frac{\gamma\,c}{1001{,}4\,(1 + 0{,}19\,c)}\right),$$

or as $\frac{RT}{1001{,}4} = 23{,}87$ is (c.f. § 4), and with $\gamma' = \frac{\gamma}{1001{,}4}$:

$$p = 23{,}87\,c\,\frac{1 - \gamma'\,c}{1 + 0{,}19\,c}\ Atm., \quad \ldots\ldots \quad (3)$$

and this is an altogether different expression from (2^b). Not only is v_1 replaced by v (which gives rise to the factor $1 + 0{,}19\,c$), but we also find $1 - \gamma'\,c$ instead of $1 - 0{,}015\,c$. In this γ' is *different for every dissolved substance*, dependent on the values of a and b, whereas the coefficient 0,015 has *the same value* for all substances dissolved in water, *independent of the nature of the dissolved substance* (c.f. § 4). Also the coefficient 0,19 depends on the dissolved substance on its molecular volume). Moreover γ' depends also on T on account

of $a : RT$. Except with H_2, where γ is negative at the ordinary temperature, γ is everywhere *positive*. But at higher temperatures its value is reversed, and becomes negative.

So, when comparing (2^b) and (3), we see clearly, that it is out of the question that the so-called osmotic pressure should follow the gas laws. Only with $c = 0$ this would be the case, but for all other values of c the deviation for the osmotic pressure is *altogether different* from that for the gas pressure. This is still more clearly pronounced, when we compare the original formulae. For the osmotic pressure viz. the equation

$$\pi = \frac{RT}{v_1}(-\log(1-x)) = \frac{RT}{v_1} x\,(1 + {}^1/_2\, x^2 + \ldots)$$

holds; for the gas pressure on the other hand:

$$p = \frac{RT}{v}\left(1 - \frac{\gamma}{v}\right),$$

so that the deviations from the gas laws (at the ordinary temperatures) are even in *opposite sense* from the deviations of the osmotic pressure for non-diluted solutions.

In view of these facts it is in my opinion no longer possible to uphold the old conception of the osmotic pressure as arising in consequence of a pressure of the molecules of the *dissolved substance* comparable with the *gas pressure*. The molecules of the dissolved substance have nothing to do with the osmotic pressure except in so far as they reduce the *water* in the solutions to *another state of concentration* (*less concentrated*), which causes the pure water (concentration 1) to move towards the water in the solution (concentration $1-x$) in consequence of the *impulse of diffusion*. On account of this a *current*, of which the *equivalent of pressure* $= \frac{RT}{v_1}(-\log(1-x))$, arises in the transition layer near the semi-permeable membrane, which current can only be checked by a *counterpressure on the solution* of equal value: the so-called *osmotic* pressure.

This is in my opinion the *only correct* interpretation of the osmotic pressure.

As I already observed on former occasions, we might just as well speak of an "osmotic" *temperature*, when the impulse of diffusion is not checked by pressure on the solution, but by *cooling* it. For at different temperatures the temperature functions C_1 (cf § 2) are no longer the same in the two members of

$$\mu_1(x, T) = \mu_1(o, T_0),$$

whereas the terms pv are now the same. In this case T would have to be $< T_0$, because the temperature exerts an opposite influence on the change of μ from the pressure.

In consequence of the term $RT\,log\,(1-x)$, $\mu_1\,(x)$ will be $< \mu_1\,(o)$. μ_1 must therefore be increased. Now $\frac{\partial \mu_1}{\partial p} = v_1$, hence *positive*, whereas $\frac{\partial}{\partial T}\left(\frac{\mu_1}{T}\right) = -\,(e_1 + pv_1)$, so *negative*. So the value of $\mu_1\,(x)$, which is too small in consequence of x, can again be made equal to that of $\mu_1\,(o)$, either by *increase of pressure* ("osmotic" pressure), or by *lowering of the temperature* ("osmotic" temperature).

It would, however, be advisable to banish the idea "osmotic pressure" altogether from theoretical chemistry, and only speak of it, when such differences of pressure are actually met with in case of semi-permeable walls (cell-walls, and such like).

6. *Appendix. Proof of some properties, mentioned in* § 2.

a. In a previous paper in these Proceedings (April 1905) I derived for $\frac{\partial v}{\partial x}$ the perfectly accurate expression [equation (4), p. 651):

$$\frac{\partial v}{\partial x} = \frac{\frac{db}{dx} - \frac{1}{RT}\frac{(v-b)^2}{v^2}\frac{da}{dx}}{1 - \frac{2a/v}{RT}\frac{(v-b)^2}{v^2}}.$$

With $\frac{db}{dx} = \beta$ and $\frac{da}{dx} = 2\alpha\sqrt{a}$, in which $\beta = b_2 - b_1$ and $\alpha = \sqrt{a_2} - \sqrt{a_1}$, this becomes:

$$\frac{\partial v}{\partial x} = \beta\frac{1 - \frac{2\alpha\sqrt{a}}{RT\beta}\frac{(v-b)^2}{v^2}}{1 - \frac{2a/v}{RT}\frac{(v-b)^2}{v^2}}.$$

And now we see at once, that this passes into β or $\frac{db}{dx}$, when

$$\underline{\beta\sqrt{a} = \alpha v},$$

For then $\frac{\alpha\sqrt{a}}{\beta}$ in the numerator becomes equal to a/v in the denominator. But when $\frac{\partial v}{\partial x} = \frac{db}{dx}$, then also $\frac{\partial^2 v}{\partial x^2} = 0$, as $\frac{d^2 b}{dx^2} = 0$, and v is a *linear* function of x.

[We above derived the condition $\beta\sqrt{a} = av$ from the general expression for $\frac{\partial v}{\partial x}$. If we knew this condition beforehand, $\frac{\partial v}{\partial x} = \frac{db}{dx}$ would immediately follow from this by differentiation, and then it would not be necessary to start from the general expression for $\frac{\partial v}{\partial x}$].

b. On p. 651 [equation (5)] of the paper cited the perfectly general expression:

$$\frac{\partial^2 \Theta}{\partial x^2} = \frac{2}{v^3} \frac{(av - \beta\sqrt{a})^2}{1 - \frac{2a/v}{RT} \frac{(v-b)^2}{v^2}}$$

was derived for $\frac{\partial^2 \Theta}{\partial x^2}$, which becomes therefore $= 0$, when again $\beta\sqrt{a} = av$. Now $\Theta = \int p dv - pv = \omega - pv$. And as $\frac{\partial^2 \Theta}{\partial x^2}$ and $\frac{\partial^2 v}{\partial x^2}$ are both $= 0$ when $av = \beta\sqrt{a}$, also $\frac{\partial^2 \omega}{\partial x^2}$ will be $= 0$, in other words ω is a *linear* function of x.

c. The heat of dilution. It is given by the formula

$$L_x = - T^2 \frac{\partial}{\partial T} \left[\frac{\mu_1(x)}{T} - \frac{\mu_1(o)}{T} \right].$$

This is viz. the so-called *differential* heat of dilution per Gr. mol. of the solvent when dn Gr. mol. solvent $\left(x = \frac{m}{m+n} \right)$ are added to a solution consisting of m Gr. mol. dissolved substance and n Gr. mol. solvent.

This becomes [see equation (1)]:

$$L_x = - T^2 \frac{\partial}{\partial T} \left[\frac{1}{T} \left\{ - \left(\omega - x \frac{\partial \omega}{\partial x} \right) + p \left(v - x \frac{\partial v}{\partial x} \right) + \omega_1 - p v_1 \right\} \right].$$

If $\frac{\partial^2 \omega}{\partial x^2} = 0$, then $\omega - x \frac{\partial \omega}{\partial x} = \omega_1$; and $v - x \frac{\partial v}{\partial x}$ will be $= v_1$, when $\frac{\partial^2 v}{\partial x^2} = 0$. But then $L_x = 0$. q. e. d.

And hence also the *total heat of mixing* will be $= 0$, when x Gr. mol. of the 2nd component are mixed with $1 - x$ Gr. mol. of the 1st component.

d. The peculiarities mentioned in § 2 under *a*, *b* and *d*, which

characterize the so-called *ideal* mixtures, are therefore *all* satisfied when

$$\underline{\beta \sqrt{a} = \alpha v.}$$

This yields:

$$\beta [\sqrt{a_1} + x\alpha] = \alpha [b_1 + x\beta],$$

when it is permissible — for liquids far from the critical temperature — to replace v by b. Hence we get:

$$\beta \sqrt{a_1} = \alpha b_1,$$

or

$$(b_2 - b_1) \sqrt{a_1} = (\sqrt{a_2} - \sqrt{a_1}) b_1,$$

or also

$$b_2 \sqrt{a_1} = b_1 \sqrt{a_2},$$

hence

$$\frac{\sqrt{a_1}}{b_1} = \frac{\sqrt{a_2}}{b_2},$$

from which we see, that the case of *ideal* mixtures occurs, when the *critical pressures* of the components have the *same* value.

e. Finally

$$\frac{\partial^2}{\partial x^2}\left(\frac{a}{b}\right) = \frac{2 (b_2 \sqrt{a_1} - b_1 \sqrt{a_2})^2}{b^3},$$

so we see that also $\frac{a}{b}$ will be a linear function of x, when $b_2 \sqrt{a_1} = b_1 \sqrt{a_2}$ or $p_1 = p_2$. In this way also c of § 2 has been proved.

(June 21, 1906).